



सत्यमेव जयते

INDIAN AGRICULTURAL
RESEARCH INSTITUTE, NEW DELHI.

L. A. R. I. 6.

MGIPC—81—6 AR/54—7-7-54—10,000.

The Journal of PHYSICAL CHEMISTRY

(Founded by Wilder D. Bancroft)

Editor

S. C. LIND

Associate Editors

E. J. BOWEN	J. R. PARTINGTON
T. R. HOGNESS	H. SCHLUNDT
C. N. HINSELWOOD	H. B. WEISER
F. H. MACDOUGALL	

Volume 40

7617
■■■■■■■■
IARI

BALTIMORE

1936

CONTENTS

NUMBER 1, JANUARY, 1936

The Constitution of Hydrous Oxide Sols from X-ray Diffraction Studies. Harry B. Weiser and W. O. Milligan	1
Electrokinetics. XVI. Streaming Potential in Small Capillaries. Henry B. Bull and Laurence S. Moyer	9
Studies on Silicic Acid Gels. VI. Influence of Temperature and Acid upon the Time of Set Charles B. Hurd	21
X-ray Spectrography of Alkali Celluloses John B. Calkin	27
The Oxide Film on Passive Iron. Wilder D. Bancroft and J. D. Porter	37
The Phase Rule in Colloid Chemistry. Wilder D. Bancroft	43
Bohmite and Bayerite. II. Lehl	47
The Diffusion Coefficient and Apparent Radius of the Cupric Ion in Silica Gels W. G. Eversole and Edw. W. Doughty	55
The Solubilities and Free Energies of Some Metallic Sulfides S. Frederick Ravitz	61
Viscosity Relationships in Emulsions Containing Milk Fat Abraham Leviton and Alan Leighton	71
Adsorption at Crystal-Solution Interfaces. VIII. Influence of Dyes and Other Organic Compounds on the Crystal Habit of Barium and Lead Nitrates. Phoebe Paine Davis and Wesley G. France	81
Observations on Polymorphism II. E. Phipps and J. H. Reedy	89
Adsorption on Chromite Catalysts J. C. W. Frazer and C. G. Albert	101
Penetration of Solar and Cosmic Rays into Fresh Water Lakes. George A. Linhart	113
Carbon Dioxide Cleavage from Dibromomalonie Acid. II. Jytte Muus	121
Molecular Dimensions from Viscosity Studies. Robert M. Theis and Henry B. Bull	125
The Production of Furfural from Xylose Solutions by Means of Hydrochloric Acid-Sodium Chloride Systems Ellis I. Fulmer, L. M. Christensen, R. M. Hixon, and R. L. Foster	133
A Method for the Determination of the Wall Correction for the Falling Sphere Viscometer. Ellis I. Fulmer and John C. Williams	143
The Effect of Certain Sugar Alcohols and their Anhydrides on the Dissociation of Boric Acid. John C. Krantz, Jr., Margarethe Oakley, and C. Jelleff Carr	151
The Radiochemical Decomposition of Deutero-ammonia. J. C. Jungers	155

NUMBER 2, FEBRUARY, 1936

The Determination of Contact Angles from Measurements of the Dimensions of Small Bubbles and Drops. I. The Spheroidal Segment Method for Acute Angles. Guilford L. Mack	159
The Determination of Contact Angles from Measurements of the Dimensions of Small Bubbles and Drops. II. The Sessile Drop Method for Obtuse Angles Guilford L. Mack and Dorothy A. Lee	169

Adsorption at Crystal-Solution Interfaces. IX. The Concentration of Foreign Substances in Solution Relative to the Quantity Adsorbed by the Host Crystal. Wesley G. France and Phoebe P. Davis	177
Spectroscopic Estimation of Adsorbed Ions. May Annetts and Lorne Newman.	187
Vapor Pressure-Water Content Relations for Certain Typical Soil Colloids. Lyle T. Alexander and M. M. Haring	195
Stream Potentials and D. c. Surface Conductivities in Small Capillaries. H. L. White, Betty Monaghan, and Frank Urban	207
Adsorption by Diatomaceous Filters. Earl J. Hoagland and John E. Rutzler, Jr	215
Adsorption and Diffusion in Zeolite Crystals. Arne Tiselius	223
The Sorption of Bromine and Iodine by Activated Charcoal. L. H. Reyerson and A. E. Cameron	233
Studies of Polarization Discharges in Multiple Electrode Systems. Herschel Hunt, Joseph F. Chittum, and Henry M. Grubb	239
The Oxidation Potential of the System Potassium Molybdocyanide-Potassium Molybdicyanide, and the Effect of Neutral Salts on the Potential. I. M. Kolthoff and Wm. J. Tomsicek	247
The Action of Potassium <i>n</i> -Amyl Xanthate on Chalcocite. A. M. Gaudin and Reinhardt Schuhmann, Jr.	257
A Study of the Sorption of Acid Sodium Oleate. R. F. Nickerson	277
New Books:	
Optical Rotatory Power. By T. Martin Lowry. Reviewed by T. S. Patterson	287
Colloid Symposium Monograph. Reviewed by S. E. Sheppard	287
Orthohydrogen, Parahydrogen and Heavy Hydrogen. By Adalbert Farkas. Reviewed by L. H. Reyerson	288
The Principles of Experimental and Theoretical Electrochemistry. By Malcolm Dole. Reviewed by Alfred L. Ferguson	288
Electrons (+ and -), Protons, Neutrons and Cosmic Rays. By Robert A. Millikan. Reviewed by S. C. Lind	289
Absolute thermische Daten und Gleichgewichtskonstante. By R. Doczekeal (in collaboration with H. Pitsch). Reviewed by J. R. Partington	290

NUMBER 3, MARCH, 1936

The Thermodynamic Properties of Cadmium Sulfate in Water-Ethyl Alcohol Solutions. Victor K. La Mer and Erwin L. Carpenter	287
The Solubility of Lead Sulfate in Aqueous Solutions of Sulfuric Acid at High Concentrations. H. D. Crockford and J. A. Addleston	303
Colloidal Solutions in Concentrated Electrolytes. Andr. Voet	307
The Solubility of Lead Bromate and its Activity Coefficients in Solutions of Electrolytes. F. H. MacDougall and Everett J. Hoffman	317
The Solubility of Lanthanum in Mercury from 0°C. to 50°C. W. George Parks and Joseph L. Campanella	333
X-ray Studies of Crystallite Orientation in Cellulose Fibers. II. Synthetic Fibers from Bacterial Cellulose Membranes. Wayne A. Sisson	343
The Influence of Denaturation on the Spreading of Proteins on a Water Surface. Hans Neurath	361
The Formation of Liesegang Rings in the Presence of Precipitates. Binayendra Nath Sen	369
Note on Thermodynamic Equilibrium in the Gravitational Field. F. O. Koenig.	373

A Comparative Method for Measuring Aqueous Vapor and Dissociation Pressures, with Some of its Applications. E. M. Collins and Alan W. C. Menzies	379
A New Electrophoresis Cell for Microscopic Observations. Margaret E. Smith and Martin W. Lisse	399
Silica Fluff. C. A. Jacobson	413
Adsorption of Radon by Glass. S. C. Lind and Robert Livingston	419
New Books:	
Origins and Development of Applied Chemistry. By J. R. Partington. Reviewed by M. Nicrenstein	421
Electron Emission and Adsorption Phenomena. By J. H. de Boer. Reviewed by Geo. Glockler	421
The Structure of Crystals. By Ralph W. G. Wyckoff. Reviewed by Geo. Glockler	422
Body Water—The Exchange of Fluids in Man. By John P. Peters. Reviewed by Ross Aiken Gortner	422
Monographien aus dem Gesamtgebiete der Mikrochemie. Farbmessungen, Theoretische Grundlagen und Anwendungen. By E. Haschek and Max Haitinger. Reviewed by I. M. Kolthoff	423
Structure and Properties of Matter. By Herman T. Briscoe. Reviewed by S. C. Lind	424
Die Bierhefe als Heil-, Nahr-, und Futtermittel. By Julius Schulin. Reviewed by A. Harden	424
The Structure of Metallic Coatings. Reviewed by J. T. Randall	425
The Eruption of Mt. Pelee, 1929-32. By Frank Perret. Reviewed by Frank F. Grout	426
Das Kristallzeichnen auf Grundlage der stereographischen Projektion. By H. Tertsch. Reviewed by F. C. Phillips	426
Wasserstoff-Ionenkonzentration (p_H). By H. Jorgensen. Reviewed by S. Glasstone	426
Journal of the Institute of Metals	427
Metallurgical Abstracts (General and Non-ferrous)	427
Gmelins Handbuch der anorganischen Chemie. Stickstoff. Reviewed by J. R. Partington	428
Eisen- und Stahllegierungen. Patentsammlung. I. Ergänzungsheft. By A. Grützner. Reviewed by J. R. Partington	428

NUMBER 4, APRIL, 1936

The Heat Capacity of Saturated Sodium Sulfate Solution. Kenneth A. Kobe and Clarence H. Anderson	429
The Thermal Dissociation of Calcium Carbonate. J. C. Southard and P. H. Royster	435
The Creeping of Saturated Salt Solutions. T. H. Hazlehurst, Jr., H. C. Martin, and L. Brewer	439
Isoelectric Point of Glycinin. R. J. Hartman and L. T. Cheng	453
The Apparent Volumes and Apparent Compressibilities of Solutes in Solution. III. Unsaturated and Supersaturated Solutions of Calcium Nitrate. Arthur F. Scott and G. L. Bridger	461
Hide Substance with Hydrogen Chloride and Ammonia. L. R. Parks and A. D. Melaven	471
An Hypothesis Concerning Bacteriophagy. John C. Williams	477

Specific Heats and Related Properties of the Binary System Methyl Alcohol-Toluene. L. S. Mason and E. Roger Washburn	481
Mixtures of Colloidal Electrolytes with Uni-univalent Salts. James W. McBain and Janet Scarles	493
Simple Kinetic Theory of Ionic Exchange. I. Ions of Equal Valency. Hans Jenny	501
The Reduction of Some Adsorbed Oxidation-Reduction Indicators. Harold A. Abramson and Ivon R. Taylor	519
The Adsorption of the Heavier Rare Gases by Mercury. Hans M. Cassel and Kurt Neugebauer	523
Tin Vanadate as a Catalyst in the Oxidation of Toluene to Benzoic Acid. Roy Huitema and O. W. Brown	531
An Experimental Test of the Identity of Electrokinetic Potentials. Electromosis and Streaming Potential Measurements with a Glass Slit. Robert DuBois and Alexander Hunter Roberts	543

NUMBER 5, MAY, 1936

A Study of Some Physical Properties of Flour Doughs in Relation to their Breadmaking Qualities. P. Halton and G. W. Scott Blair	561
Liquid Ammonia as a Solvent. V. Metallic Solutions. Joseph F. Chittum and Herschel Hunt	581
The Flocculation of the Stannic Oxide Sols. H. S. Van Klooster and A. Petrovich	591
Liesegang Rings of Manganese Sulfide. II. Olin F. Tower	599
Activation of Redwood and Ash-free Sugar Charcoal in a Current of Air. James W. McBain and R. F. Sessions	603
The Mechanism of the Photochemical Reaction between Bromine and Water. H. Armin Pagel and Warner W. Carlson	613
The Dielectric Constants of Solutions of Some Organic Acids in Ethyl Alcohol and Benzene. Robert C. Gore and H. T. Briscoe	619
The Physical Properties of the Ternary System Ethyl Alcohol-Glycerin-Water. R. C. Ernst, C. H. Watkins, and H. H. Ruwe	627
Mixed Crystal Formation of Zinc Sulfide Postprecipitated with Mercuric Sulfide. The Aging of Mercuric Sulfide and of Zinc Sulfide. R. Moltzau and I. M. Kolthoff	637
Quantitative Analyses of Liesegang Rings. A. T. Lincoln and John C. Hillyer	645
The Solubility and Activity Coefficient of Silver Acetate in Mixed Solvents. F. H. MacDougall and Charles Edward Bartsch	649
The Physical Chemistry of Flotation. VII. Trimethylcetylammmonium Bromide as a Flotation Agent. Ian William Wark	661
The Reactivity of Halogen Compounds. II. The Rates of Reaction and the Energies of Activation of 2,4-Dinitrochlorobenzene with Aromatic Primary Amines. Attar Singh and D. H. Peacock	669
Studies on Molecular Weight Changes of Sulfur Monochloride. W. A. Patrick and N. Hackerman	679
Ferric Sulfate in Aqueous Solutions of Other Sulfates. F. K. Cameron	689
New Books:	
The Next Hundred Years: the Unfinished Business of Science. By C. C. Furnas. Reviewed by S. C. Lind	697
Electrolytic Oxidation and Reduction: Inorganic and Organic. By S. Glass-tone and A. Hickling. Reviewed by I. M. Kolthoff.	697
Inorganic Colloid Chemistry. II. The Hydrous Oxides and Hydroxides. By H. B. Weiser. Reviewed by L. H. Reyerson	698

Colorimetric Methods of Analysis. By Foster Dee Snell and Cornelia T Snell. Reviewed by E. B. Sandell	699
Ueber katalytische Verursachung im biologischen Geschehen. By Alwin Mittasch. Reviewed by P. Haas	699
Les Solutions Concentrées. Théorie et Applications aux Mélanges Binaires de Composés Organiques. By Jean Timmermans. Reviewed by F. H. MacDougall	699
Solubility of Non-electrolytes. By Joel H Hildebrand. Reviewed by F. H MacDougall	700
Die Fermente und ihre Wirkungen. By Carl Oppenheimer. Reviewed by Ross Aiken Gortner	700
Fundamentals of Biochemistry in Relation to Human Physiology. By T. R Parsons. Reviewed by Howard B Lewis	700
Flame. By O. C. deC. Ellis and W. A. Kirkby. Reviewed by J. R. Partington	701
Aluminium-Legierungen. By A. Grutzner and G. Apel. Reviewed by J. R. Partington	701
Gmelins Handbuch der anorganischen Chemie. Stickstoff. Reviewed by J. R. Partington	701
Gmelins Handbuch der anorganischen Chemie. Aluminium. Reviewed by J. R. Partington	702
Reactions of Organic Compounds. By W. J. Hickinbottom. Reviewed by R. J. W. Le Fèvre	702

NUMBER 6, JUNE, 1936

On the U-tube Method of Measuring Electrophoresis. A. L. Roberts and J. C. Carruthers	703
The Viscosity of Sodium Amalgams. Henry E. Bent and Norman B. Keevil	709
The Determination of Surface Conductance from Measurements on Suspensions of Spherical Particles. Hugo Fricke and Howard J. Curtis	715
Hydrogen Bridges in Ice and Liquid Water. Maurice L. Huggins	723
The Diffusion of Copper Sulfate in Aqueous Solutions of Sulfuric Acid. A. F. W. Cole and A. R. Gordon	733
A Preliminary Study of the Absorption Spectra of Cephalin, Lecithin, and Selected Antigens. Augustus Wadsworth and M. O'L. Crowe	739
A Study of the Laws Governing the Cation-exchanging Properties of a Precipitated Aluminum Silicate. R. Charles Bacon	747
Cathode Polarization as a Function of the Current Density in Fused Salts. S. Karpatschoff and O. Poltoratska	763
Oxidation Processes at the Cathode. O. K. Kudra and K. N. Ivanov	769
The Postprecipitation of Zinc Sulfide with Mercuric Sulfide. I. M. Kolthoff and R. Moltzau	779
The Physical Chemistry of Flotation. VIII. The Process of Activation. Elsie Evelyn Wark and Ian William Wark	799
The Relationship between Conditions Governing Rupture and Flow in Flour Doughs. P. Halton and G. W. Scott Blair	811
Soaps: Electric Charge Effects and Dispersing Action. W. M. Urbain and L. B. Jensen	821
Optical Difficulties with the Cylindrical Cataphoresis Cell. A. M. Buswell and T. E. Larson	833
Surface Spreading and Surface Solution of Positively Adsorbed Substances. T. F. Ford	835

A Comparison of the Glass and Quinhydrone Electrodes for the Measurement of the Activity of the Hydrogen Ion in Sucrose Solutions. H. P. Cady and J. D. Ingle	837
The Activity Coefficients of Lithium Chloride and Potassium Iodide in Ethyl Alcohol by the Boiling-point Method. J. N. Pearce and M. L. McDowell	845
Note to the Editor: The Optical Activity of Camphor in Alcoholic Solutions	853
New Books:	
The Phenomena of Polymerisation and Condensation. Reviewed by J. T. Randall	855
Fluorescence Analysis in Ultra-violet Light. By J. A. Radley and Julius Grant. Reviewed by J. H. Mathews	855
Collected Scientific Papers of Sir William Bate Hardy, F. R. S. Reviewed by Ross Aiken Gortner	856
Adsorptionstechnik. By Franz Krzil. Reviewed by H. Freundlich	857
Lehrbuch der physikalischen Chemie. By K. Jellinek. Reviewed by J. R. Partington	858
Textbook of Quantitative Inorganic Analysis. By I. M. Kolthoff and E. B. Sandell. Reviewed by C. H. Schiflett	858
Inorganic Chemistry. By N. Bjerrum, translated by R. P. Bell. Reviewed by W. Wardlaw	859
Die Interferenzen von Rontgen und Elektronenstrahlen. By M. von Laue. Reviewed by J. T. Randall	860
Veröffentlichungen aus dem Kaiser Wilhelm-Institut für Silikat Forschung in Berlin-Dahlem. Reviewed by J. T. Randall	860
Chemical Discovery and Invention in the Twentieth Century. By Sir William A. Tilden. Reviewed by Lillian Cohen	860
Molekülspektren und ihre Anwendung auf chemische Probleme. By H. Sponer. Reviewed by W. Jevons	861

NUMBER 7, OCTOBER, 1936

X-ray Diffraction Studies of Chitin, Chitosan, and Derivatives. George L. Clark and Albert F. Smith	863
Alteration of the Free Surface Energy of Solids. I. Vertical-rod Method for the Measurement of Contact Angles and Preliminary Study of Effect of Heat Treatment on Magnitude of Contact Angles. F. E. Bartell, J. L. Culbertson, and Mike A. Miller	881
Alteration of the Free Surface Energy of Solids. II. Effect of Heat Treatment of Metals in Air. F. E. Bartell and Mike A. Miller	889
Alteration of the Free Surface Energy of Solids. III. Effect of Heat Treatment of Metals in a Vacuum and in Several Gases. F. E. Bartell and Mike A. Miller	895
The Solubility Relationships in Mixtures of Brassidic Acid with Erucic Acid, Methyl Brassidate, and Ethyl Brassidate. I. J. P. Keffler and A. M. Maiden	905
Addition Compounds of Phosphorous Acid with Certain Organic Compounds. H. L. Redfield and G. B. King	919
A Further Study of the Effect of Sugar Alcohols and their Anhydrides on the Dissociation of Boric Acid. John C. Krantz, Jr., C. Jelleff Carr, and Frances F. Beck	927
New Books:	
Kolloidik. Eine Einführung in die Probleme der modernen Kolloidwissenschaft. By A. v. Buzágh. Reviewed by N. K. Adam	933

Reports on Progress in Physics. Reviewed by J. R. Partington	933
Gmelins Handbuch der anorganischen Chemie. Aluminium. Reviewed by J. R. Partington	934
Gmelins Handbuch der anorganischen Chemie. Uran und Isotope Reviewed by J. R. Partington.	934
Stereoscopic Drawings of Crystal Structures. Edited by M. von Laue and R. von Mises; drawings by E. Rehbock-Verständig; text by G. Menzer. Reviewed by R. W. James.	934
Eclipses of the Sun. By S. A. Mitchell. Reviewed by W. J. Luyten	935
Abridged Scientific Publications from the Kodak Research Laboratories. Reviewed by Robert Livingston	936
Physical Aspects of Organic Chemistry. By William A. Waters. Reviewed by Alberto F. Thompson, Jr	936
The Theory of Emulsions and their Technical Treatment. By William Clayton. Reviewed by C. Robinson	936
The Nature of Physical Theory. By P. W. Bridgman. Reviewed by Robert Livingston	937
Differential Equations in Applied Chemistry. By Frank Lauren Hitchcock and Clark Shove Robinson. Reviewed by F. H. MacDougall	937
Fundamental Experiments in Chemistry. By E. D. Goddard. Reviewed by J. R. Partington	937
Kurzgeschichte der Chemie. By F. Ferchl and A. Sussenguth. Reviewed by J. R. Partington	938
Tables of Physical and Chemical Constants and Some Mathematical Functions. By G. W. C. Kaye and T. H. Laby. Reviewed by J. R. Partington	938
Recent Advances in Organic Chemistry. By A. W. Stewart, with four new chapters by H. Graham. Reviewed by E. E. Turner	938
Physical Chemistry. By Frank H. MacDougall. Reviewed by T. R. Hogness	939
Elementary Principles in Physical Chemistry. By T. J. Webb. Reviewed by T. R. Hogness	940

NUMBER 8, NOVEMBER, 1936

An Electronic Analysis of Some Surfaces by Means of Slow Electrons. Robert J. Moon and William D. Harkins	941
Polymolecular Films: Mixed Films with Two or More Components. I. Fatty Acids and Non-polar Substances. Robert J. Myers and William D. Harkins	959
The Application of the High-speed Motion Picture Camera to Research on the Surface Tension of Liquids. E. A. Hauser, H. E. Edgerton, B. M. Holt, and J. T. Cox, Jr	973
Unimolecular Films of Nerve Proteins. Lyman Fount and Francis O. Schmitt	989
Transference Numbers of Colloidal "Ferric Hydroxide." James W. McBain and Winifred McClatchie Thomas	997
Diffusion Study of Dyes. Samuel Lenher and J. Edward Smith	1005
Catalysis of Ionic Oxidation-Reduction Reactions by Dyes and its Probable Mechanism. P. A. Shaffer	1021
Adsorption on Ionic Lattices. I. M. Kolthoff	1027
The Gelation of Bentonite Suspensions. Geoffrey Broughton and Lombard Squires	1041
The Adsorption of Complex Ammonio Ions by Silica Gel. L. H. Reyerson and R. E. Clark	1055

Factors Influencing Adsorption at Surfaces of Red Cells. Betty R. Monaghan and H. I. White	1063
The Mechanism of the Coagulation of Sols by Electrolytes. VI. Cupric Ferrocyanide Sol. Harry B. Weiser and W. O. Milligan	1071

NUMBER 9, DECEMBER, 1936

The Adsorption Condenser and Electromotive Force. Joseph F. Chittum and Herschel Hunt	1083
The Direct Examination of Sols by X-ray Diffraction Methods. W. O. Milligan and Harry B. Weiser	1095
The Polymeric Character of Bituminous Coal. H. C. Howard	1103
Molecular Properties of Lignin Solutions from Viscosity, Osmotic Pressure, Boiling-point Raising, Diffusion, and Spreading Measurements. D. I. Loughborough and Alfred J. Stamm	1113
The Colloidal Nature of Asphalt as Shown by its Flow Properties. R. N. Traxler and C. E. Coombs	1133
Particle Size and Optical Properties of Emulsions. Emerson D. Bailey, J. Burton Nichols, and Elmer O. Kraemer	1149
Ultrafiltration through Cellophane of Porosity Adjusted between Colloidal and Molecular Dimensions. James W. McBain and R. F. Stuewer	1157
Studies in Thixotropy. I. Development of a New Method for Measuring Particle-size Distribution in Colloidal Systems. E. A. Hauser and C. E. Reed	1169
Adsorption of Ions and the Physical Character of Precipitates. II. Ferric Oxide and Bentonite Precipitates. G. E. Cunningham, H. E. Gabler, and W. S. Peachin	1183
Coacervation of Amylophosphoric Acid and Proteins. P. Koets	1191
Kelvin Single-potential Differences. Wilder D. Bancroft and Jermain D. Porter	1201
Sedimentation Volume, Dilatancy, Thixotropic and Plastic Properties of Concentrated Suspensions. H. Freundlich and A. D. Jones	1217

THE CONSTITUTION OF HYDROUS OXIDE SOLS FROM X-RAY DIFFRACTION STUDIES¹

HARRY B. WEISER AND W. O. MILLIGAN

Department of Chemistry, The Rice Institute, Houston, Texas

Received June 20, 1935

Sols of the hydrophobic type which includes most of the hydrous oxides, can be prepared fairly free from electrolytes, but it was demonstrated first by Thomas Graham and confirmed repeatedly thereafter, that in the absence of protecting colloids some electrolyte must be present in the sols to ensure their stability. Thus ferric oxide sol formed by hydrolysis of ferric chloride or by peptization of the hydrous oxide by ferric chloride always contains traces of chloride however long the dialysis is continued.²

The presence of chloride in the dialyzed sols led Wyruboff and Verneuil (13) to suggest that the various preparations contain basic salts or chlorides of "condensed" hydroxides. This idea was further extended and developed by several investigators especially by Duclaux (3), Malfitano (7), Hantzsch and Desch (4), and Linder and Picton (6). Thus, the constitution of the sols was represented by formulas such as:



Pauli (8) considers the colloidal particles to be complex ions resulting from ionization of complex electrolytes allied to the Werner compounds. Since the constitution of a given sol varies with the conditions of preparation he represents it by a general formula. In the case of ferric oxide sol this is



in which $x = 32$ to 350 and $y = 4$ to 5.7 in sols formed by hydrolysis. It is difficult to justify this formulation, since no one has established the existence of $\text{Fe}(\text{OH})_3$, and FeOCl is obtained only under special conditions in a bomb tube at elevated temperatures.

Thomas and coworkers (9, 10) suggest that the dispersed phase in

¹ Presented at the Twelfth Colloid Symposium, held at Ithaca, New York, June 20-22, 1935.

² Sorum sols (J. Am. Chem. Soc. **50**, 1264 (1928)) containing no detectable chloride either contain a trace of some other electrolyte or are protected by some material derived from the dialyzing membrane during the prolonged dialysis.

7617

hydrous oxide sols, such as alumina sol formed by peptization of the gel with hydrochloric acid, consists of olated and possibly oxolated aluminum oxychloride complexes of the Werner type resembling the poly-ol basic chromic salts formulated by Bjerrum (2). Thomas formulates one such hypothetical complex as given in figure 1. The assumption that such hypothetical compounds exist in the sol was made to account for the observation that the pH value of the sol is raised by the stepwise addition of neutral electrolytes, the anion order being: oxalate > acetate > sulfate > halides > nitrate. The increased pH value was attributed to replacement of the OH groups by the anion of the added salt, followed by the union of the displaced OH radicals with hydrogen to form water.

Since hydrous oxide sols formed in the presence of chloride, say, always contain more or less chloride, Thomas believes that such sols should be designated as metallic oxychloride sols rather than as hydrous oxide sols. He recognizes that the term ferric oxychloride hydrosol is objectionable,

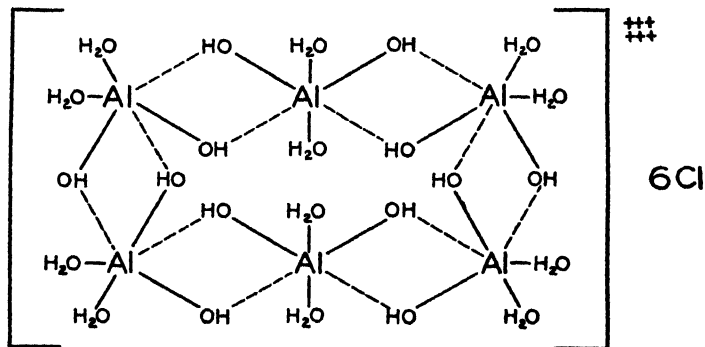


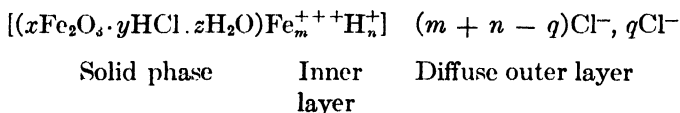
FIG. 1. Formula of a hypothetical alumina complex (after Thomas)

since it connotes a definite chemical compound when no such meaning is intended. Nevertheless he prefers to regard the hydrous oxide sols as oxysalt sols, since the colloidal particles are not pure hydrous oxides. To be consistent, one should rename the metallic sols and the salt sols, which, like the oxide sols, are not pure insoluble metal or salt. It is difficult to see what would be gained by introducing such a change in our terminology. The ratio of iron to chlorine in a ferric oxide sol has been variously reported as 6, 42, 84, 396, 2700, and higher. To designate a sol with a low chloride content as an oxychloride sol is like calling precipitated barium sulfate a chlorosulfate because it contains some adsorbed barium chloride.

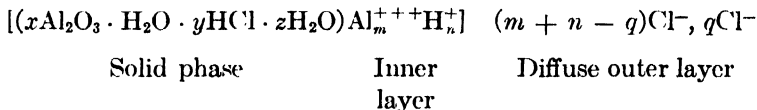
It is now quite generally recognized that the stability of a positive silver halide sol is due to the preferential adsorption of silver ion by unsaturated secondary valence forces on the surface of the crystals. The crystals will also contain some adsorbed silver nitrate. Similarly a hydrous oxide sol formed in the presence of metallic chloride, hydrochloric acid, and their

corresponding ions will contain varying amounts of the several components, depending on the precise method of formation and the purification of the sol. The positive charge on a given sol is due to the preferential adsorption of hydrogen and metallic ion on the surface of the hydrous oxide just as the positive charge on a silver halide sol is due to preferential adsorption of silver ion. It is unnecessary to attribute the charge to the presence of an "ionogenic complex attached to the surface" (Pauli) unless the presence of such a complex has been rendered highly probable. Thus to assume the presence of even a simple salt like FeOCl in a ferric oxide sol goes well beyond the established facts.

In recent years investigations (11) have been made of the various phenomena which take place on adding electrolytes stepwise to sols of the hydrous oxides of iron and aluminum. To account for the several phenomena, including the form of the chloride displacement curves and of curves showing the change in pH value, the constitution of the particles may be represented by the general formulas:



and,



Iver (5) accepts this formulation of the constitution of certain oxide sols, but suggests that the outer portion of the double layer contains hydroxyl ions as well as chloride ions. The displacement of the former on titrating with neutral salts would account for the increase in the pH value of the mixture. It seems rather questionable, however, whether hydroxyl ions will be present in the outer portion of the double layer in sols having a pH value of 4 to 5. The increase in the pH value on the addition to the sols of neutral salts, especially those with multivalent anions, is doubtless due to the increase in adsorption of hydrogen ion in the presence of a strongly adsorbed anion. This increased adsorption of cations in the presence of strongly adsorbed anions is a general phenomenon that has been observed with various types of adsorbents such as carbon and fibers as well as with the hydrous oxides. With salts such as citrate, oxalate, and acetate, buffer action increases the pH value of the sol-electrolyte mixture above that of the sol alone.

From the evidence obtained by potentiometric titration of the sols, there would appear to be no necessary reason for assuming that the sols are

colloidal electrolytes consisting of basic salts or Werner complexes. On the contrary the indirect evidence suggests that the solid phase consists essentially of the hydrous oxide (or simple hydrate).

Since x-ray diffraction studies have proven helpful in determining the composition of gels, it was believed that similar studies on sols might give direct evidence of the constitution of the colloidal particles in the sols. The chief complication in the examination of the systems is the relatively low concentrations of the solid phase and the scattering of the x-rays by the water in the samples. Böhm and Niclassen (1) showed that the gels from certain oxide sols were not amorphous; but in most cases it was not stated whether the air-dried or moist gel was examined. Since Thomas believes that the elements of water in certain oxide sols are combined in the form of poly-ol basic Werner salts, it is not permissible to air-dry the samples before examination. On the contrary, the sols must be studied directly, or the undried gel, obtained preferably by ultrafiltration of the sols, must be examined. Preliminary experiments were carried out with sols of the hydrous oxides of aluminum, tin, and indium.

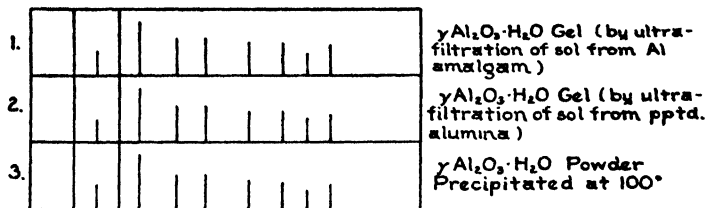


FIG. 2. X-ray diffraction patterns

ALUMINUM OXIDE SOLS

Two sols of aluminum oxide were employed. The first was prepared by peptization, with hot 0.01 *N* hydrochloric acid, of the gel formed by the action of amalgamated aluminum on water. The method of Thomas (10) was used except that the gel was not dried. The second sol was obtained by peptization, with hot 0.05 *N* hydrochloric acid, of the gel thrown down from hot aluminum chloride solution with ammonia and washed by decantation until almost free from chloride. In both cases a large excess of the gel remained unpeptized, from which the sol was decanted. After standing quietly for several days to allow further traces of unpeptized gel to settle, the slightly cloudy sols were examined.

Portions of the sols were ultrafiltered through a cellophane membrane, and the resulting moist gels were analyzed by the x-ray diffraction method, using a camera of the Seemann-Bohlin type. Copper radiation filtered through nickel foil, at 60 milliamperes and 50,000 volts, was employed. Under these conditions but five to ten minutes exposure was necessary, so that little or no drying of the gel took place. The results of the observa-

tions are shown in diagram form in figure 2 (1 and 2). For the purpose of comparison the diagram of $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ powder is included in the figure. Reproductions of the negatives are shown in figure 3. From these observa-

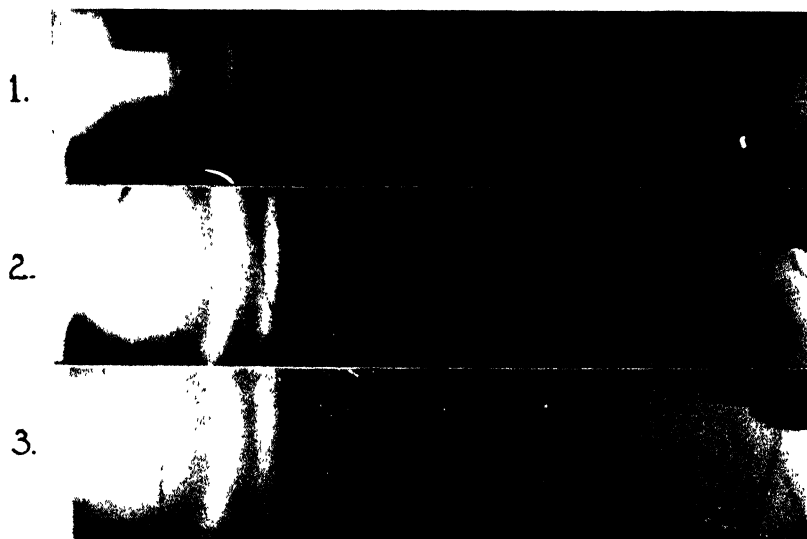


Fig 3 X-ray diffraction patterns

- 1 $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ gel (ultrafiltration of sol from aluminum amalgam)
- 2 $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ gel (ultrafiltration of sol from precipitated alumina)
- 3 $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ powder (precipitated at $100^\circ\text{C}.$)

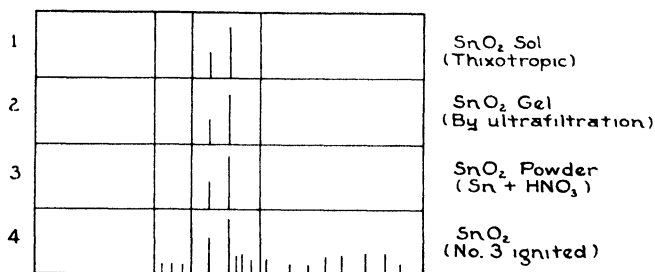


Fig 4. X-ray diffraction patterns

tions, it would appear that the particles in the alumina sol consist essentially of hydrous $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$. There is no reason to believe that they are made up of simple basic salts or basic salts of the Werner type.

STANNIC OXIDE

Stannic oxide sol was prepared by the method of Zsigmondy (14). Twenty-five grams of hydrated stannic chloride was dissolved in 20 liters

of water and allowed to hydrolyze. The resulting gel was washed until the wash-water was free from chloride. After suspending in 250 cc. of water, it was peptized with three drops of concentrated ammonia and the resulting sol was boiled to remove excess ammonia. The moist gel obtained by ultrafiltration of the clear sol gave the x-ray diffraction pattern of anhydrous stannic oxide or cassiterite, as shown diagrammatically in figure 4 (2). For the purpose of comparison the patterns of the so-called " β "-stannic oxide and of anhydrous stannic oxide are included in the diagram.

The sol concentrated to 100 cc. became thixotropic. This sol gave the pattern shown in figure 4 (1).

INDIUM OXIDE SOL

A solution of indium nitrate was precipitated in the cold with ammonia, the precipitate thoroughly washed, and peptized in the cold with dilute hydrochloric acid. The gel obtained by ultrafiltration of the sol gave the



FIG. 5. X-ray diffraction patterns for $\text{In}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ gel (from ultrafiltration of sol)

x-ray diffraction pattern shown in figure 5. This is the pattern for $\text{In}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ or $\text{In}(\text{OH})_3$ (12).

From the above x-ray studies, it would appear that the particles in typical oxide sols consist essentially of aggregates of minute crystals of hydrous oxides or of simple oxide hydrates. In the sols containing chloride, the latter is not bound in the form of a basic salt in most cases, but is adsorbed in an amount depending on the size and physical character of the particles. Such sol systems are properly referred to as hydrous oxide sols.

In the light of the above, if one prefers to regard the hydrous oxide sols as electrolytes with colloidal ions it must be emphasized that there is a fundamental difference between sols and non-colloidal complex electrolytes such as potassium ferrocyanide, the cobalt amines, the complex platonic salts, etc., formulated by Werner. There is also a distinct difference between a hydrous oxide sol and such colloidal electrolytes as the soaps and Congo red, in that the latter contain ionic micelles made up of groups of ions which have a definite composition and which carry one charge for each equivalent of the ion, whereas the micelles of the former have no definite

composition and may carry hundreds or thousands of equivalents for each free charge.

SUMMARY

X-ray diffraction examination of the moist gels from typical hydrous oxide sols indicates that the particles of the solid phase in such sols consist essentially of aggregates of minute crystals of hydrous oxides or of simple oxide hydrates. In the sols containing chloride, the latter is not bound in the form of a basic salt in most cases, but is adsorbed in an amount depending on the size and physical character of the particles.

REFERENCES

- (1) BOHM AND NICLASSEN: *Z. anorg. Chem.* **132**, 7 (1924).
- (2) BJERRUM: *Z. physik. Chem.* **73**, 724 (1910).
- (3) DUCLAUX: *J. chim. phys.* **5**, 79 (1907); **7**, 405 (1909).
- (4) HANTZSCH AND DESCH: *Ann.* **323**, 38 (1902).
- (5) IVER: *Proc. Indian Acad. Sci.* **1**, 372 (1934).
- (6) LINDER AND PICTON: *J. Chem. Soc.* **87**, 1919 (1905).
- (7) MALFITANO: *Compt. rend.* **148**, 1047 (1909); *Z. physik. Chem.* **68**, 232, 248 (1910).
- (8) PAULI AND VALKO: *Elektrochemie der Kolloide*. Julius Springer, Vienna (1929).
- (9) THOMAS AND WHITEHEAD: *J. Phys. Chem.* **35**, 27 (1931).
THOMAS AND VON WICKLEN: *J. Am. Chem. Soc.* **56**, 794 (1934).
- (10) THOMAS AND TAI: *J. Am. Chem. Soc.* **54**, 841 (1932).
THOMAS AND VARTANIAN: *J. Am. Chem. Soc.* **57**, 4 (1935).
- (11) WEISER: *J. Phys. Chem.* **35**, 1, 1368 (1931).
WEISER AND GRAY: *J. Phys. Chem.* **36**, 2178 (1932).
- (12) WEISER AND MILLIGAN: *X-ray Studies on the Hydrous Oxides. VIII. Gallium, Indium, and Thallic Oxides*. Reported at the Meeting of the American Chemical Society, April, 1935.
- (13) WYROUBOFF AND VERNEUIL: *Bull. soc. chim.* [3] **21**, 137 (1899).
- (14) ZSIGMONDY: *Ann.* **301**, 361 (1898).

ELECTROKINETICS. XVI

STREAMING POTENTIAL IN SMALL CAPILLARIES¹

HENRY B. BULL AND LAURENCE S. MOYER²

Division of Agricultural Biochemistry, University of Minnesota, St. Paul, Minnesota

Received June 20, 1935

The applicability of the conventional equation of streaming potential to small capillaries is an important subject. It involves the whole question of streaming potential through membranes, and accordingly should be of particular interest to the biologist. Smoluchowski (13) showed that membranes were subject to the same mathematical treatment he employed for single capillaries and, within the limits of the restrictions, the equations held for capillaries of any size or shape. His equation for streaming potential is

$$\zeta = \frac{4\pi\eta KH}{DP} \quad (1)$$

where ζ is the electrical potential across the double layer, η is the coefficient of viscosity, K is the specific conductance of the streaming liquid, H is the streaming potential, D is the dielectric constant, and P is the pressure forcing the liquid through the capillary.

A marked decrease in the streaming potential has been demonstrated by Bull and Gortner (5) with diaphragms made of fine quartz particles. The effect became apparent with particles slightly below $200\ \mu$ in diameter and rapidly became more important, until at $5\ \mu$ the streaming potential was only 25 per cent of that for the $200\ \mu$ particles. The decrease in potential with the smaller particles is no doubt due to the smaller capillaries. Their data, however, offer no easy way of determining the capillary size. White, Urban, and Krick (16) also found a diminishing streaming potential with decreasing capillary size. The question arises as to the critical size of a capillary below which the simple theory of Smoluchowski is no longer adequate. There are several factors to be considered.

¹ Presented at the Twelfth Colloid Symposium, held at Ithaca, New York, June 20-22, 1935.

Published as Paper No. 1353, Journal Series, Minnesota Agricultural Experiment Station.

² National Research Fellow in the Biological Sciences.

It was first realized by Stock (14) that surface conductance must be considered and that the specific conductance used in equation 1 was that of the liquid in the membrane or small capillary. An involved mathematical treatment has been given by Cole, Bikerman, Komagata, and others (1). As shown by Briggs (3), the difficulty is easily taken care of experimentally by determining the cell constant of the membrane with $N/10$ potassium chloride; then by determining the resistance of the membrane containing the various solutions, the specific conductivity of the liquid in the membrane (K_s) is easily calculated, and this K_s then replaces the K of equation 1. This, then, presents no serious difficulty for the streaming potential technique in small capillaries.

In the derivation of the streaming potential equation (13), Poisson's equation is integrated for the case of two parallel plates, and the resulting equation applies only when the thickness of the double layer is small in comparison with the radius of the capillary. We are really dealing, however, with two coaxial cylinders whose edges are the thickness of the double layer apart. The electrical potential between these cylinders is

$$\zeta_1 = \frac{4\pi\sigma}{D} r \ln \left(1 + \frac{\lambda_c}{r} \right) \quad (2)$$

where r is the radius of the inside cylinder, D is the dielectric constant, λ_c is the distance between the cylinders, and σ^3 is the charge per cm.² When $r \gg \lambda_c$, this equation reduces to that for two parallel plates.⁴

$$\zeta_2 = \frac{4\eta\sigma}{D} \lambda_p \quad (3)$$

The ratio of these two potentials is

$$\frac{\zeta_1}{\zeta_2} = \frac{r}{\lambda_p} \ln \left(1 + \frac{\lambda_c}{r} \right) \quad (4)$$

Except where there is overlapping of the double layers, $\lambda_p = \lambda_c$. Estimation of the critical radius from values of r/λ_p must be done by an approximation (11). If $z_i\zeta < 25$ millivolts (where z_i is the valence of an ion of the i^{th} type),

$$\lambda_p = \frac{1}{\kappa} = a \quad (5)$$

³ Throughout this portion of the discussion, σ is considered constant.

⁴ Since $\ln \left(1 + \frac{\lambda}{r} \right) = \frac{\lambda}{r} - \frac{\lambda^2}{2r^2} + \frac{\lambda^3}{3r^3} - \dots$

where λ_p is the mean thickness of the double layer when equation 3 holds,

$$\kappa = \sqrt{\frac{4\pi N^2 \epsilon^2}{DRT}} \sqrt{\sum c_i z_i^2} \quad (\text{Debye-Hückel}) \quad (6)$$

and

$$a = \sqrt{\frac{DRT}{4\pi N^2 \epsilon^2 (z_i + z_j) c_i z_i \text{ (or } c_j z_j)}} \quad (\text{Gouy}) \quad (7)$$

N = Avogadro's number, R = the gas constant, $c_i, (c_j)$ = ionic concentration in moles per cubic centimeter (1, 9, 11).

The ratio, ξ_1/ξ_2 , may be considered as a measure of the deviation from the conventional streaming potential equation. In figure 1 (curve A) this ratio is shown plotted against the capillary radius divided by the thickness of the double layer. It will be noted that a 10 per cent deviation is encountered at a ratio of pore radius to double layer thickness of about 4.

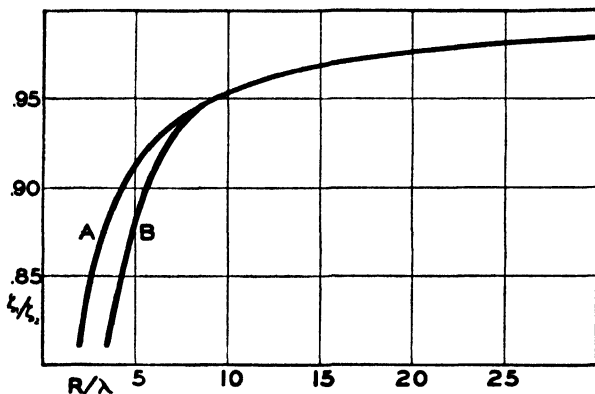


FIG. 1. Diminution in ξ produced by small values of r/λ from equations 4 and 9

Recently Lens (9) investigated the thickness of the double layers between two parallel plates by the use of the Gouy theory. He calculated that in thin slits an interference of the two double layers exists, causing the centers of gravity of the charges in the double layers to be pushed in toward the walls of the slit. He derived the following equation expressing the relation between the thickness of the layer and the half-width of the slit:

$$\lambda_c = a - \frac{r}{e^{r/a} - 1} \quad (8)$$

Calling the half-width of the slit r , we have substituted this value of λ_c in equation 2 and divided by equation 3, thus obtaining the following equation:

$$\frac{\xi_1}{\xi_2} = \frac{r}{\lambda_p} \ln \left[1 + \frac{a}{r} - \frac{1}{(e^{r/a} - 1)} \right] \quad (9)$$

Again ζ_1/ζ_2 is plotted against r/λ_p as shown in curve B, figure 1.⁵ The values of ζ_1/ζ_2 represent the deviation from the ideal case of a plane surface with no interference. A 10 per cent deviation is encountered in this case at $r/\lambda_p = 6$. While it is perhaps forcing the point to substitute the equation of Lens, which was derived for two parallel planes, into that involving cylinders, we believe the result serves as a first approximation. Table 1, column 2, shows the capillary size which would give rise to a 10 per cent deviation in ζ for various concentrations of a uni-univalent salt (assuming $z_1\zeta < 25$ millivolts (11)).

Komagata (8) has derived expressions showing the influence of capillary size on the streaming potential. By making the Debye-Hückel approximation (1) ($\sin h \psi F/RT \cong \psi F/RT$), he has integrated the fundamental equation of electrokinetics (1),

$$\nabla \cdot \nabla \psi = \frac{\partial^2 \psi}{\partial x^2} = \frac{1}{x} \frac{\partial \psi}{\partial x} = \kappa^2 \psi \quad (10)$$

for the case of a cylindrical capillary. He arrives at an expression involving J_0 and J_1 , Bessel functions of the zero-th and first order and of the first kind,

$$\psi = -\Psi \frac{J_0(ikx)}{J_1(ikr)} \quad (11)$$

where Ψ is the true ζ -potential, x is the coördinate (in the cylindrical system) coinciding with the radius, r , and ψ is the potential at any point on x .

From this, the equation for σ ,

$$\sigma = \frac{D\Psi\kappa i J_1(ikr)}{4\pi J_0(ikr)} \quad (12)$$

is developed. This reduces to equation 3 for large values of κr .^{6, 7}

Komagata then develops the streaming potential equation after the conventional method (13) and substitutes these values to attain the following equation for streaming potential:

$$H = \frac{PD(-\Psi)}{4\pi\eta K_s} \left(1 - \frac{2[-iJ_1(ikr)]}{\kappa r J_0(ikr)} \right) \quad (13)$$

⁵ In plotting, the assumption was made that $a = \lambda_p = \frac{1}{\kappa}$.

⁶ Since $\lim_{r \rightarrow \infty} J_0(ikr) = \frac{e^{ikr}}{\sqrt{2\pi ikr}} = \lim_{r \rightarrow \infty} -iJ_1(ikr)$

⁷ We are indebted to Dr. Komagata for a personal communication with regard to this point.

By comparing equation 1 with this,

$$|\pm\Psi| = f\zeta \quad (14)$$

where

$$\frac{1}{f} = 1 - \frac{2[-iJ_1(ikr)]}{krJ_0(ikr)} \quad (15)$$

Komagata has calculated limiting values for r , at different concentrations of electrolyte, at which a deviation of 10 per cent between Ψ and ζ

TABLE 1

Limiting values of radii, corresponding to concentrations of uni-univalent electrolyte, at which a 10 per cent diminution in ζ should be observed

CONCENTRATION IN MOLES PER LITER	LIMITING RADIUS IN μ FROM EQUATION 9 ($kr = 6$)	LIMITING RADIUS IN μ FROM EQUATION 14 ($kr = 20$)
10^{-7}	5.78	19.5
10^{-6}	1.83	6.2
10^{-5}	0.578	1.95
10^{-4}	0.183	0.62
10^{-3}	0.0578	0.195

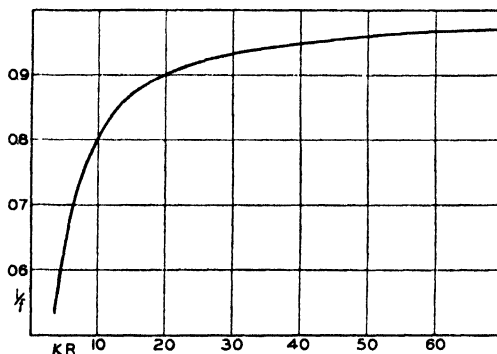


FIG. 2. Equation 15 from the theory of Komagata

should be observed (ref. 8, p. 36). Unfortunately, the decimal point has been misplaced in this table, so that these values are ten times what they should be. Correct values are listed in table 1, column 3. The critical point for a deviation of this magnitude lies at $kr = 20$.

The reciprocal of the factor f (equation 15) has been plotted against kr in figure 2 (after Komagata). On comparing figure 1 with figure 2, it will be seen that the factor f , which represents $\zeta_{\text{cylinder}} \div \zeta_{\text{plane}}$, and the ratios of equations 4 and 9 change in an inverse direction as kr varies. When kr is large, ζ_1/ζ_2 in equations 4 and 9 reduces to unity and so does f (in equation 14). But at small values of kr , equation 12 does not reduce to

equation 2. In the case of the ratios calculated from the cylindrical and plate condensers (equations 4 and 9), the factor by which the observed ζ (from equation 1) is multiplied is always < 1 ; in Komagata's equations, it is always > 1 . This fundamental difference may reside in the fact that in the first treatment σ was assumed to be constant with changing r and the influence of thickness of the double layer predominant. In Komagata's treatment σ changes with r . The effect of equations 4 and 9 is to reduce ζ ; Komagata's equation 13 tends to eliminate the observed lowering in streaming potential with decreasing r .

In the above connection, Bikerman (2) has derived an expression for the current produced by the streaming potential in slits and takes the ionic atmosphere into consideration. He finds that the width of the slit plays a rôle only when it is comparable in size to the thickness of the double layer.

Another factor which must be considered in the treatment of small capillaries is that of viscosity. Terzaghi (15) gives empirical equations expressing the viscosity of water as a function of the width of narrow slits. He found that

$$\frac{\eta}{\eta_0} = 1 + \frac{6.02 \times 10^{-42}}{S^8} \quad (16)$$

to

$$\frac{\eta}{\eta_0} = 1 + \frac{2.42 \times 10^{-43}}{S^8} \quad (17)$$

where η_0 is the viscosity of water at 25°C. and η is the viscosity of water in a slit of width $2S$ at the same temperature. Terzaghi worked with membranes of clay. Figure 3 shows the change of viscosity with the half-width of the slit. Equations 16 and 17 are plotted as curve 2 and curve 1 (figure 3), respectively. It is clear that an appreciable change in viscosity is found at a radius of about 9×10^{-6} cm., and thereafter it increases very rapidly. Deriagin (6), likewise, reports that water exhibits rigidity when placed between glass surfaces less than 150μ apart. The one surface formed the bottom of a vessel; the other was a convex glass lens which was forced to oscillate about a vertical axis. The distance between the two was measured by observing Newton's fringes. It was found that the rigidity vanished above 150μ , which is, as he remarks, in the same order of magnitude as reported by Terzaghi. The viscosity effect would invalidate streaming potential measurements made much below a capillary radius of 10^{-5} cm. In membranes of mixed pore sizes, pores below this value would be virtually inoperative in contributing to the streaming potential.

Electrosmotic effects resulting from the streaming potential must also be considered. This so-called back pressure has been discussed by Bull (4) and Reichardt (12). There is as yet no unanimity of opinion in this

respect. It is possible to regard this problem in another way than has yet been done. We can, for example, compare in a very simple and direct fashion the maximum electrical work obtained with the total mechanical work done on a liquid streaming through a diaphragm.

The electrical work per unit time = H^2/R_T joules per second, where H is the streaming potential across the diaphragm in volts, and R_T is the total resistance in the system in ohms. The mechanical work per unit time = $1 \times 10^{-7} VP$ joules per second, where V is the volume in cubic centimeters per second and P is the pressure in dynes per unit area.

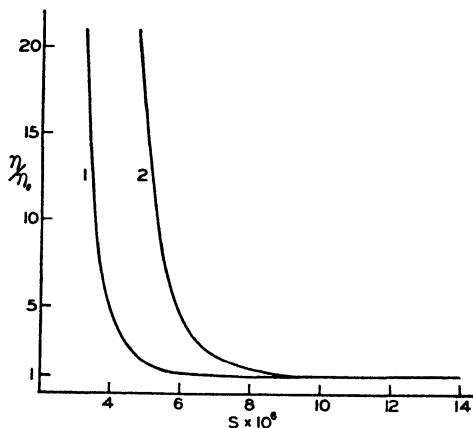


FIG. 3. Changes in the viscosity of water produced by small pore diameters

Dividing the electrical work by the mechanical work, we obtain,

$$\frac{\text{Electrical work}}{\text{Mechanical work}} = 1 \times 10^7 \frac{H^2}{VPR_T} \quad (18)$$

Now if we assume that we are dealing with cylindrical capillaries, we may substitute from Poiseuille's law the value for V ,

$$V = \frac{\pi Pr^4 n}{8\eta l} \quad (19)$$

where r is the average radius of the capillaries, n is the number of capillaries of radius r , and l is the average length of the capillaries.

Also, we have the electrical resistance,

$$R_T = \frac{l}{\pi K_s r^2 n} \quad (20)$$

Substituting these expressions for V and R_T we have

$$\frac{\text{Electrical work}}{\text{Mechanical work}} = \frac{8H^2 \eta K_s}{P^2 r^2} \times 10^7 \quad (21)$$

Since both the electrical work and mechanical work are done over the same distance and area, we may write

$$\frac{\text{Electrical pressure}}{\text{Mechanical pressure}} = \frac{8H^2\eta K_s}{P^2r^2} \times 10^7 \quad (22)$$

This confirms in a satisfactory manner the previous equation of Bull (4), since we obtain

$$\frac{P_1}{P} = \frac{8H^2\eta K_s}{P^2r^2} \times 10^7 \quad (23)$$

by dividing the electrical "Gegendruck," P_1 ,

$$P_1 = \frac{8\eta K_s H^2}{Pr^2}$$

by the applied (mechanical) pressure and converting from electrostatic to practical units.

If we are dealing with a given solution, η is a constant and, as a first approximation, K_s and H/P are constants. The ratio of the "Gegendruck" to the mechanical pressure varies as the reciprocal of the radius squared. In general, K_s , due to the surface conductivity, increases as the radius decreases, while H/P decreases with decreasing radius in accord with earlier sections of this paper. We hope to investigate equation 22 experimentally in the near future.

The following calculations illustrate the use of equation 18. The diaphragm was of finely powdered quartz about 5μ in diameter. A $2 \times 10^{-4} N$ sodium chloride solution was streamed through the diaphragm. The following data were obtained: (1) resistance across diaphragm = 7.05×10^{-4} ohms; (2) pressure forcing liquid through diaphragm = 10.5 cm. Hg = 1.40×10^5 dynes cm.^{-2} ; (3) E.M.F. across diaphragm = 8.10×10^{-2} volts; (4) rate of flow of solution through diaphragm = 7.20×10^{-3} cc. per second.

Substituting in equation 18,

$$\frac{\text{Electrical work}}{\text{Mechanical work}} = \frac{(8.10 \times 10^{-2})^2 \times 10^7}{7.20 \times 10^{-3} \times 1.40 \times 10^5 \times 7.05 \times 10^{-4}} = 9.24 \times 10^{-4}$$

This shows that in this case back-pressure effects could not interfere with the flowing of the liquid. Results of this same type were obtained from calculations based on measurements made with cellulose diaphragms.

The peculiar results obtained by Bull and Gortner (5) with diaphragms made of heterogeneous-sized quartz particles, where a break in the straight-line relationship between the streaming potential and the pressure was observed at about 25 cm. of mercury pressure, are still unexplained

and are apparently inexplicable on the basis of any of the above calculations. This indicates that there are other factors to be considered. These broken lines are, however, only obtained with very close packing, so that this unknown factor or factors need only be considered with capillaries where such broken lines are observed.

During the course of these investigations we were disturbed by the lack of a suitable method for determining the pore radius; although the method of Erbe (7) was tried, it was found not wholly satisfactory for our purposes. We finally solved our difficulties in the following fashion.

By substituting equation 20 in Poiseuille's law (equation 19) and replacing $K.R_r$ by C , the cell constant of the diaphragm (3), we have

$$r = \sqrt{\frac{8\eta CV}{P}} \quad (24)$$

This equation rests on the assumption (as, in general, with all methods for determining radii) of cylindrical capillaries; results obtained from it are

TABLE 2

Average pore radii of various diaphragms measured in electrolyte solutions at concentrations not affecting rate of flow

MATERIAL	SALT	NORMALITY	RADIUS IN μ	CHARACTERISTICS
Quartz	KCl	10^{-2}	29.9	163 μ particle diameter
Quartz	KCl	10^{-2}	20.6	128 μ particle diameter
Quartz. . . .	NaCl	$> 4 \times 10^{-1}$	1.38	ca. 5 μ particle diameter (mixed)
Cellulose.. .	MgCl ₂	10^{-4}	0.98	Gave normal ζ -concentration curve
Cellulose....	NaCl	0 to 2×10^{-3}	0.86	Cf. figure 4
Cellulose...	BaCl ₂	0 to 2×10^{-3}	0.86	Cf. figure 4 (same membrane)

therefore subject to error but serve to characterize any particular membrane and represent, essentially, the rate of flow through that membrane. It is believed that the correct order of magnitude, at least, can be obtained by this method.

We applied equation 24 to the calculation of pore radii in several diaphragms and obtained the results shown in table 2. Comparing table 2 with table 1, it will be seen that the mean pore radii of the cellulose diaphragms are above the critical radius for concentrations of 10^{-4} N or greater.

Cellulose prepared from Schleicher and Schüll filter paper after the method of Briggs (3) was packed into a diaphragm. This was the same cellulose preparation as used by Bull and Gortner. As shown in figure 4, no variation in rate of flow (i.e., average radius) was noted in any of the electrolyte solutions (sodium chloride and barium chloride) used, in the

range 0 to $2 \times 10^{-4} N$. Values for ζ in sodium chloride solutions are also plotted in figure 4 from the data of Bull and Gortner and of Briggs. As may be seen, no significant difference between the two sets of data can be noted, although each is based on a different cellulose preparation and a different membrane. The whole problem of the critical radius for cellulose diaphragms will be discussed in a later paper (10).

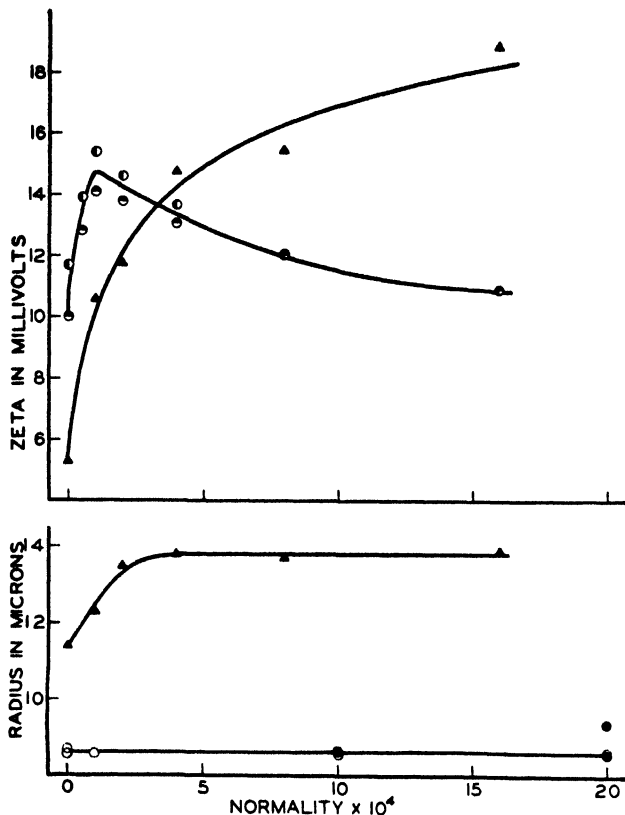


FIG. 4. Comparison of ζ -concentration and radius-concentration curves of a cellulose diaphragm and a diaphragm of quartz below the critical pore size. Triangles, quartz; circles, cellulose. \bullet , barium chloride solutions; \circ , sodium chloride solutions; \odot , data of Bull and Gortner; \ominus , data of Briggs. The ζ values for quartz are plotted at half-scale.

It is interesting to note that the pore radius for quartz of 163μ diameter was 31.8μ (table 2) and for those particles 128μ in diameter the average radius was 22.2μ . Bull and Gortner (5) found the critical radius for $2 \times 10^{-4} N$ sodium chloride to lie between these two radii. This is surprising, as it is much above that predicted by Komagata (0.43μ). The explanation possibly lies in the fact that Komagata's equations are

derived on the assumption that $z\zeta < 25$ millivolts, while actually the potential in this case is about 82 millivolts. White, Urban, and Krick (16) found the critical radius to be about 10μ for $5 \times 10^{-4} N$ potassium chloride streaming through glass capillaries. This high critical radius may, no doubt, be traced to the same cause as discussed above, for glass likewise has a high ζ -potential.

Values for the mean pore radii observed with a diaphragm of small quartz particles below the size found critical by Bull and Gortner are plotted as a function of the sodium chloride concentration in figure 4. Constancy is reached at a concentration of $4 \times 10^{-4} N$. Incidentally, the rate of flow is independent of time and shows no blocking effects such as those noted with cellophane membranes. This constant value persists at least up to a concentration of $N/10$. It probably represents the true mean pore radius. In all cases, the rate of flow was a linear function of the applied pressure.

The ζ -concentration curve for this quartz diaphragm in sodium chloride (calculated by equation 1) is also shown in figure 4. It will be noted that the usual maximum observed by Briggs (3), Bull and Gortner, and others (see especially Abramson, ref. 1, p. 207) at $10^{-4} N$, in the case of uni-univalent electrolytes, is absent here; the curve progresses steadily upward. Values of ζ were approximately 30 per cent of those observed above the critical limit (1, 5). This suggests that membranes which exhibit a maximum at the usual concentration ($10^{-4} N$) are not in the critical range.

SUMMARY

Conditions in a membrane have been considered in relation to the measurement of the streaming potential and the following subjects are discussed:

1. The equation for the potential between two coaxial cylinders has been substituted for the conventional plate condenser equation in the case of small pore radii.
2. Lens' modification of the thickness of the double layer in thin slits has been introduced into this equation, and the critical value of the radius has been estimated by this method.
3. These equations have been compared with the critical radius calculated from Komagata's equations. It is found that the two sets of equations do not yield concordant results except when the radius is large.
4. The change in the viscosity of water with capillary size has been considered.
5. The electrical "Gegendruck" has been compared with the mechanical pressure, and an equation expressing this relationship has been derived.
6. A method for obtaining the average pore radius has been developed

and tested. The theoretical critical pore radius has been compared with those actually found in diaphragms; the two values do not agree in the case of quartz and glass.

7. Anomalies are noted in the ζ -concentration and flow-concentration curves of quartz diaphragms with pores below the critical point; these curves are compared with cellulose, which behaves in a normal manner.

We wish to take this opportunity to thank Professor R. A. Gortner for his encouragement and helpful suggestions throughout the course of these investigations.

REFERENCES

- (1) ABRAMSON, H. A.: *Electrokinetic Phenomena*. The Chemical Catalog Co., Inc., New York (1934).
- (2) BIKERMAN, J. J.: *Z. physik. Chem.* **163A**, 378 (1933).
- (3) BRIGGS, D. R.: *J. Phys. Chem.* **32**, 641 (1928).
- (4) BULL, H. B.: *Kolloid-Z.* **60**, 130 (1932).
- (5) BULL, H. B., AND GORTNER, R. A.: *J. Phys. Chem.* **36**, 111 (1932).
- (6) DERIAGIN, B. V.: *Physik. Z. Sowjetunion* **4**, 431 (1933).
- (7) ERBE, F.: *Kolloid-Z.* **63**, 277 (1933).
- (8) KOMAGATA, S.: *Researches of the Electrotech. Lab. Tokyo*, No. 362 (1934).
- (9) LENS, J.: *Proc. Roy. Soc. London* **139A**, 596 (1933).
- (10) MOYER, L. S., AND BULL, H. B.: *J. Gen. Physiol.*, **19**, 239 (1935).
- (11) MÜLLER, H.: *Cold Spring Harbor Symposia on Quantitative Biology* **1**, 1 (1933).
Long Island Biological Association, Cold Spring Harbor.
- (12) REICHARDT, H.: *Z. physik. Chem.* **166A**, 433 (1933).
- (13) SMOLUCHOWSKI, M. VON: *Bull. acad. sci. Cracovie* **A**, p. 182 (1903).
- (14) STOCK, J.: *Anz. Akad. Wiss. Krakau* **A**, p. 635 (1912).
- (15) TERZAGHI, C.: *Z. angew. Math. Mech.* **4**, 107 (1924); *J. Rheol.* **2**, 253 (1931).
- (16) WHITE, H. L., URBAN, F., AND KRICK, E. T.: *J. Phys. Chem.* **36**, 120 (1932).

STUDIES ON SILICIC ACID GELS. VI

INFLUENCE OF TEMPERATURE AND ACID UPON THE TIME OF SET¹

CHARLES B. HURD

Department of Chemistry, Union College, Schenectady, New York

Received June 20, 1935

INTRODUCTION

In a study of the setting of silicic acid gels in this laboratory, Hurd and Letteron (1) have noted an interesting relation between the "time of set" of the gel mixture and the temperature. They found that the logarithm of the time of set could be represented as a linear function of the reciprocal of the absolute temperature. By making certain rather simple assumptions and treating the process as a chemical reaction, they were able to calculate the value of an energy term analogous to the "heat of activation." The values for several series of different mixtures of solutions of sodium silicate and acetic acid gave the average value 16,940 calories. This was, of course, within the range for chemical reactions.

This result was so interesting that it was decided to run a careful check upon the constancy of this value. In the study reported by Hurd and Miller (2) using several different brands of sodium silicate, with soda-silica ratios ranging from 1:3.86 to 1:2.00, a close agreement in the values for this heat of activation was discovered. With six different series, each of five different silicates, variations of not over 2 per cent in this heat of activation were found. The average value was found to be 16,640 calories. We considered at that time that a sufficiently exhaustive study had been made of the effect of temperature upon time of set of these mixtures involving acetic acid.

The constancy of this quantity for these gels of sodium silicate-acetic acid mixtures has suggested an investigation involving other acids. It would be very interesting to check the constancy of the same quantity for other acids and to compare the values for the different acids. In this way an idea could be obtained as to whether this quantity is the same for any acid-sodium silicate mixture, or varies according to the acid employed. In this paper will be found the results of a study involving comparisons of four possible acids.

¹ Presented at the Twelfth Colloid Symposium, held at Ithaca, New York, June 20-22, 1935.

EXPERIMENTAL

In any study of the setting of silicic acid gels, the factors of temperature and hydrogen-ion concentration play a very important part. The latter has been discussed, among others, by Prasad and Hattiangadi (4) and Hurd, Raymond, and Miller (3). As the latter have pointed out, the time of set is proportional to the concentration of hydrogen ions for concentra-

TABLE 1

Time of set of gel mixtures using different acids

Concentration of NaOH = 0.386 gram-mole per liter. Concentration of SiO₂ = 0.636 gram-mole per liter

NO.	CONCENTRATION OF ACID IN GRAM-MOLES PER LITER	pH	TIME OF SET IN MINUTES AT		
			25.1°C.	38.4°C	53.0°C.
Series I. Acetic acid					
1	0.496		54.5	15.0	4.4
2	0.621		109.5	31.0	9.0
3	0.844		194.5	57.0	15.8
4	1.041		266.5	84.0	23.3
5	1.240		322.0	97.5	28.8
Series II. Tartaric acid					
1	0.414	4.62	75.5	19.0	5.5
2	0.440	4.45	146.0	42.5	10.8
3	0.466	4.25	228.0	70.5	19.5
4	0.518	4.01	415.0	118.0	34.5
Series III. Citric acid					
1	0.500	5.16	27.0	7.4	2.2
2	0.625	4.57	90.5	25.5	8.0
3	0.750	4.21	195.5	56.0	17.3
4	0.875	3.92	341.0	96.5	31.0
Series IV. Succinic acid					
1	0.502	5.31	25.0	7.5	2.1
2	0.564	5.04	43.0	13.0	3.5
3	0.627	4.87	65.5	18.0	5.6
4	0.690	4.74	87.5	24.4	7.5

tions of the latter from 10^{-4} to 10^{-6} . It is possible to duplicate the hydrogen-ion concentration in an acid mixture of solutions of sodium silicate and acetic acid, owing to buffering effect of the sodium acetate formed, and with sufficiently close agreement merely by mixing measured volumes of the solutions of sodium silicate and acetic acid. Such a thing is, of course, completely impossible with any strong acid. In that case a more complicated technique must be employed.

The work to be described includes a study of all the weak acids found suitable. The acid must be sufficiently weak so that the hydrogen-ion control is satisfactory. It must be sufficiently soluble at 25°C. The acids found suitable were acetic, tartaric, citric, and succinic. The ionization constants are 1.8×10^{-5} , 1.1×10^{-3} , 8×10^{-4} , and 6.6×10^{-5} for the first hydrogen at 25°C. Monobasic and polybasic acids are represented.

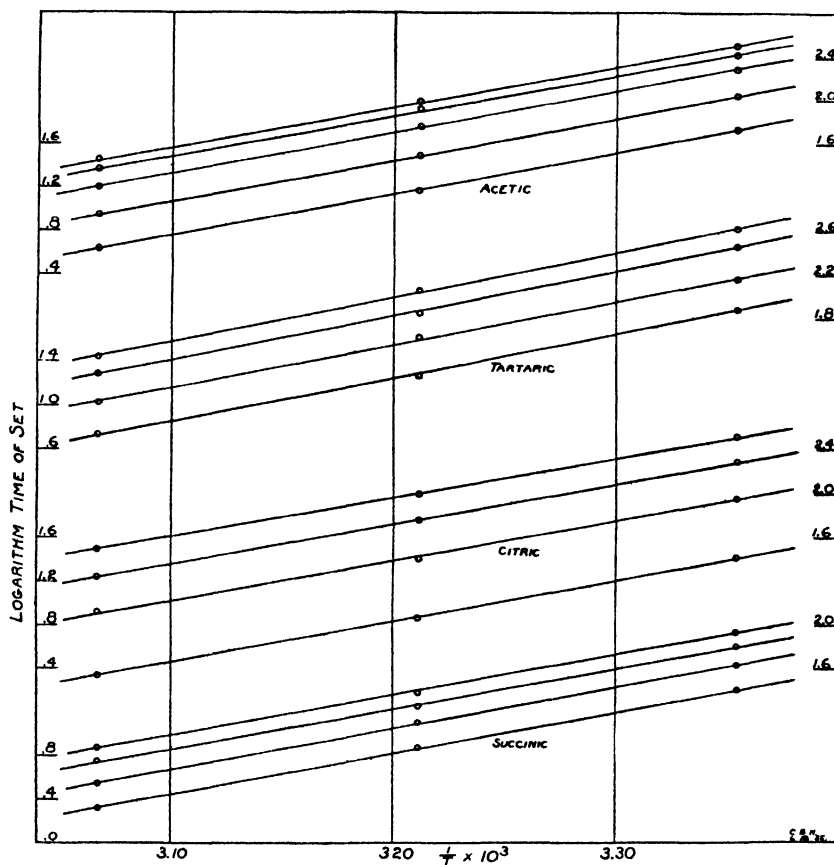


FIG. 1. Effect of temperature on time of set of silicic acid gels with different acids

It is to be regretted that boric acid was not available because of its low solubility.

Mixtures were made as previously described in this series of papers. The silicate used was E brand² with a soda-silica weight ratio of 1:3.19.

² The authors wish to thank the Philadelphia Quartz Company for its kindness in supplying all the silicate used in this and other research.

All distilled water was freshly boiled to eliminate carbon dioxide. Standard chemically pure reagents were used.

Mixtures were run at three different temperatures in carefully controlled water thermostats. The mixtures of 80 cc. were thermostated in covered 100-cc. Griffin form Pyrex beakers. The time of set was determined by the "tilted rod" method. Check determinations were always run, agreement in time to 2 per cent or less being obtained. It should be noted that in these containers at the highest temperature, the temperature of the gel mixtures remained a fraction of a degree below the temperature of the

TABLE 2

Values for the slope of the curves for log time of set against reciprocal absolute temperature

MIXTURE	ACID			
	Acetic	Tartaric	Citric	Succinic
1	3820	3920	3720	3700
2	3780	3890	3700	3780
3	3790	3750	3680	3780
4	3680	3760	3700	3740
5	3650			

TABLE 3

Values for the heat of activation for the setting of silicic acid gels with certain weak acids

MIXTURE	ACID			
	Acetic	Tartaric	Citric	Succinic
1	17500	17950	17020	16950
2	17300	17800	16950	17300
3	17350	17170	16850	17300
4	16850	17220	16950	17230
5	16720			
Average.....	17140	17530	16940	17190

bath. The gel mixture temperature was recorded. The data are given in table 1, the times of set being the average of several determinations.

These data were plotted, using the logarithm of the time of set as ordinate with the reciprocal of the absolute temperature as abscissa. The curves obtained are apparently linear. Figure 1 shows the type of graph obtained. It should be noted that the ordinates have been adjusted to permit the four curves to be plotted on the same drawing. In obtaining the slopes, of course, each set of curves was plotted separately, obtaining steeper lines and better accuracy.

The slope was determined from the curves obtained. The values of the

slopes are given in table 2. By multiplying the slope of the curves by $2.303R$, the heat of activation should be obtained. Those values are included in table 3.

DISCUSSION

The data presented here and in the previous work of Hurd and Miller show certain characteristics which are worthy of discussion. The calculated heats of activation are essentially constant for a given acid. It must be remembered that the best results which we have been able to secure for the time of set, after six years of work, show differences up to 2 per cent. At higher temperatures evaporation causes an error which we are unable to avoid with our method of determining the time of set. The heat of activation is determined from the slope of a curve. To secure better results would require a very long series of determinations, such as were reported by Hurd and Miller for acetic acid mixtures. A complete series of runs should be performed at 0°C . We have carried out enough of these for the acids discussed in this paper to convince us that our reported results are correct.

A comparison of the values for a given acid will show an appreciable decrease in the heat of activation as one goes down the series for each acid. This was apparent in the more accurate data on acetic acid reported by Hurd and Miller, and is apparent in the data reported here for acetic and tartaric acids. A comparison of the average results shows an appreciable difference in the value for the different acids.

In the study of the reaction of iodine and acetone, catalyzed by various acids, Rice and his coworkers (5, 6) and Rice and Urey (7) have reported that the heat of activation is decreased somewhat by the addition of a salt of the acid catalyst, when a weak acid is used. Our results do not show this effect, but do show a somewhat lower heat of activation in the case of acetic and tartaric acids as more acid is used.

They have also reported that their reaction showed a lower temperature coefficient for weak acids than for strong acids. The same general effect is shown here, tartaric acid having the highest heat of activation and also the highest dissociation constant, although the differences are not particularly marked.

A striking difference between the effect of the acid should be noted between the reaction studied by Rice and his coworkers and the setting of the silicic acid gels. In the iodine-acetone reaction, the acid serves as a catalyst. In the setting of gels of silicic acid in the acid range, the presence of more acid retards the setting of the gel.

We can give no explanation at present for the similarity and differences of these results.

SUMMARY

The effect of temperature upon the time of set of gels of silicic acid, made by mixing solutions of sodium silicate with solutions of acetic, tartaric, citric, or succinic acids, has been studied.

The heats of activation are essentially constant.

The heat of activation is slightly higher for the strongest acid, tartaric acid.

REFERENCES

- (1) HURD AND LETTERON: J. Phys. Chem. **36**, 604 (1932).
- (2) HURD AND MILLER: J. Phys. Chem. **36**, 2194 (1932).
- (3) HURD, RAYMOND, AND MILLER: J. Phys. Chem. **38**, 663 (1934).
- (4) PRASAD AND HATTIANGADI: J. Indian Chem. Soc. **6**, 893 (1929).
- (5) RICE AND KILPATRICK: J. Am. Chem. Soc. **45**, 1401 (1923).
- (6) RICE AND LEMKIN: J. Am. Chem. Soc. **45**, 1896 (1923).
- (7) RICE AND UREY: J. Am. Chem. Soc. **52**, 95 (1930).

X-RAY SPECTROGRAPHY OF ALKALI CELLULOSES¹

JOHN B. CALKIN

Dennison Manufacturing Company, Framingham, Massachusetts

Received June 20, 1935

Bancroft and Calkin (1) have determined previously the true amounts of sodium hydroxide and water taken up by cotton. They suggested a correlation between these data and the x-ray data on ramie of other investigators. In another paper (2) it was shown that the caustic soda might be taken up in three ways, i.e., by formation of a solid solution, by adsorption, or by the formation of a sodium cellulosate which would be adsorbed by the cellulose.

In order to clarify this situation, it is important to have the adsorption data and x-ray data on the same sample. The present investigation deals with the correlation of x-ray data with the previous work.

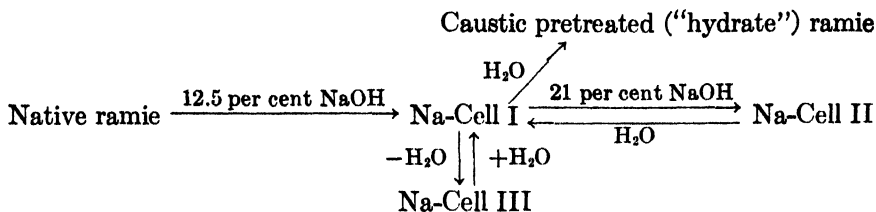
From an x-ray point of view, ramie is the best material to work with as it gives the best diffraction patterns. However it is difficult to purify, so that adsorption studies have been made on cotton. For this reason, the x-ray data presented here have been obtained on cotton. It is hoped at a later time to purify ramie, determine the amounts of caustic soda and water taken up, and relate the x-ray data to this. The work on cotton and ramie will then present the background for attacking the problem from the organic viewpoint, in order to write the formulas.

Hess and coworkers have been investigating the alkali cellulose problem by means of x-rays. They have recently obtained data on the total amounts of caustic soda and water taken up by ramie (6) by an indirect neutral salt method worked out previously (9, 10). It has been shown (2) that this type of indirect method presents difficulties, and the centrifuge method is therefore considered more reliable (1).

Before describing the experimental results, it appears best to acquaint the reader with certain experimental evidence arrived at by Susich and Wolff (11) and Hess and Trogus (5). The former have investigated the changes occurring when ramie is treated with caustic soda, and the subsequent difference after washing out the caustic soda. The latter have discussed the different x-ray diagrams resulting when caustic soda (and other

¹ Presented at the Twelfth Colloid Symposium, held at Ithaca, New York, June 20-22, 1935.

alkalis) are left in the ramie. The following scheme shows what occurs:



Hess and Trogus found that when ramie fibers were treated with 16 per cent sodium hydroxide and the solution allowed to remain in the fibers a new diagram resulted, which they ascribed to the formation of Na-Cell I. By desiccating Na-Cell I, they obtained another diagram, that of Na-Cell III, which, in the presence of water, reversed to Na-Cell I. With about 21 per cent caustic soda in the sample they obtained the diagram of Na-Cell II, which did not change on dehydration and reversed to Na-Cell I on the addition of sufficient water. In approaching any modification, the transition did not occur sharply at a given concentration but gradually, that is to say, in the case of the change of native ramie to Na-Cell I, the native diagram was present in a mixed diagram (native and Na-Cell I) approximately over a 3 per cent range. Susich and Wolff have found that the washed-out product yields still another diagram, the "hydrate" or "mercerized" diagram. When cellulose with this latter diagram is treated with caustic soda it gives the same diagram with the caustic in the sample as native fiber treated with caustic soda of the same concentration. When the caustic is subsequently washed out and the fiber dried, the diagrams are the same.

CHANGES IN THE X-RAY PATTERN

Figure 1, reproduced from another paper (1), gives the amounts of caustic and water taken up. It was desired to determine whether or not the x-ray pattern was changed completely at the point of maximum water. In order to determine at what point the x-ray pattern of cotton changed, samples of cotton were treated in caustic soda solution for twenty-four hours at 25°C. The samples were then washed caustic-free, after which they were air-dried. X-ray patterns of the fibers were taken, and it was found, as shown by the data in table 1, that the native pattern begins to change at about 12.8 per cent and is changed completely between 14.3 and 14.4 per cent sodium hydroxide. As will be seen by consulting figure 1, this practically coincides with the place where maximum water is taken up and where the horizontal portion of the change-in-titer (Vieweg) curve comes.

When the caustic soda solution is allowed to remain in the fibers and the

x-ray diagram obtained,² it is found that a new diagram, that of the product known as Na-Cell I, is obtained. Using cotton the limit for the formation of Na-Cell I is between 13.4 and 14.1 per cent sodium hydroxide, as shown in table 2.

It has been shown previously that the up and down curves with cotton are not the same (see figure 2). For this reason it was believed that the change to Na-Cell I, using mercerized cotton, should occur at a lower concentration than with native cotton. This is the case for, as the data in table 3 show, the limit with cotton pretreated with 14.4 per cent sodium hydroxide is between 10.8 and 11.85 per cent.

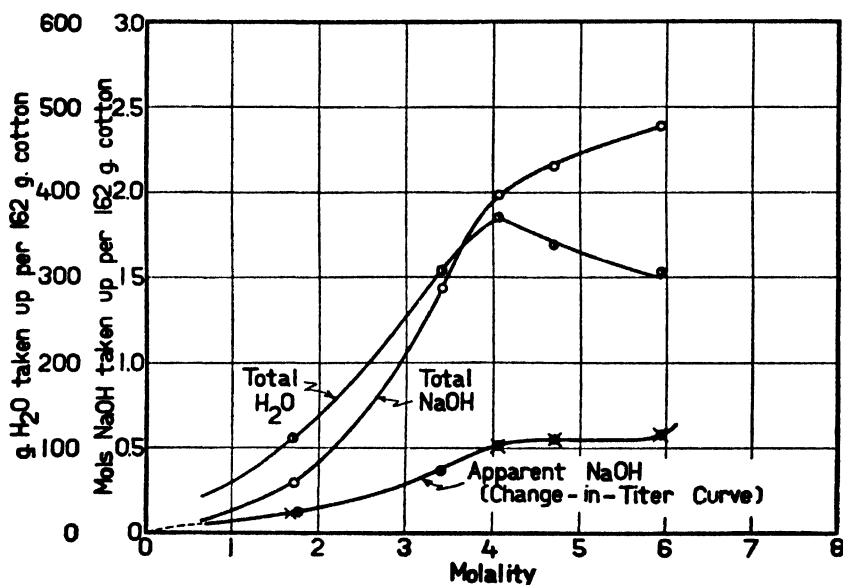


FIG. 1. Sodium hydroxide and water taken up by cotton

Trogus has shown (12) that a greater amount of hydrazine is taken up by cellulose fibers in dilution series than in concentration series, and that the

² Diagrams were obtained in the usual Keesom tubes. A variation from the usual procedure was our method of putting the sample in the tube. A sample of cotton was centrifuged for a given length of time, then the sample for the Keesom tube was pulled out in the usual way. The sample was held by one person and then another person tied one end with fine thread which had been previously threaded through a tube. The ends held by the fingers were then cut off, and the sample was pulled into the tube. The tube was then sealed with wax. Heat was not used because of the danger of drying or scorching the sample. The above method for placing the sample in the tube worked very well after some practice, and the writer is indebted to Dr. Russel for his assistance.

change in x-ray pattern occurs at a lower concentration. From these results of Trogus, our sorption results with various up (concentration) and down (dilution) series shown in figure 2, and our present x-ray results, it is evident that a dilution series from, say, 14 to 15 per cent would lower the limit given in table 3 still further.

Trogus also claims the formation of Na-Cell III' at low concentration by dilution series from Na-Cell I and by concentration series from pretreated (hydrate) cellulose at 2.65 per cent sodium hydroxide. As shown in table 3, this was not checked with cotton. As Trogus worked with ramie, it was decided to use ramie, but Na-Cell III' was not checked, as shown in table 4.

TABLE 1

X-ray pattern of native cotton, pretreated for twenty-four hours at 25°C. and washed

CONCENTRATION OF PRETREATMENT	RESULTING X-RAY PATTERN
<i>per cent</i>	
10.3	Native cellulose
12.8	Mostly native, but slight mercerized
13.32	Native and mercerized about equal
14.3	Mostly mercerized, but slight native
14.38	Mercerized

TABLE 2

Effect of caustic solution upon native cotton

CONCENTRATION OF NaOH	RESULTING X-RAY PATTERN
<i>per cent</i>	
6.9	Native cotton
11.09	Native cotton
13.4	Almost pure Na-Cell I; some native
14.1	Na-Cell I

Trogus does not give the concentration of pretreatment but this should not explain the difficulty, as he started with mercerized cellulose. At present, the reason for the discrepancy is not clear.

Cellophane takes up little if any alcohol, and hence should not be appreciably plasticized in alcoholic caustic solution (2). On this basis one should be able to obtain the effect of sodium hydroxide alone on the x-ray pattern. Standard cotton was placed in a concentrated solution of alcoholic caustic soda at room temperature (ca. 23°C.) for twenty-four hours. The change-in-titer amount of caustic taken up was found to be 0.92 mole of sodium hydroxide per mole of cellulose at an outside concentration of 2.35 moles of sodium hydroxide per 1000 grams of ethyl alcohol. The cotton was then neutralized in water-free acidulated (hydrochloric acid) alcohol, and then washed chloride-free with distilled water. The sample was air-

dried, and an x-ray pattern of a bundle of parallel fibers obtained. The spacings obtained were those for native cellulose, showing that the taking up of caustic soda from alcohol in caustic soda solution does not change the diagram.

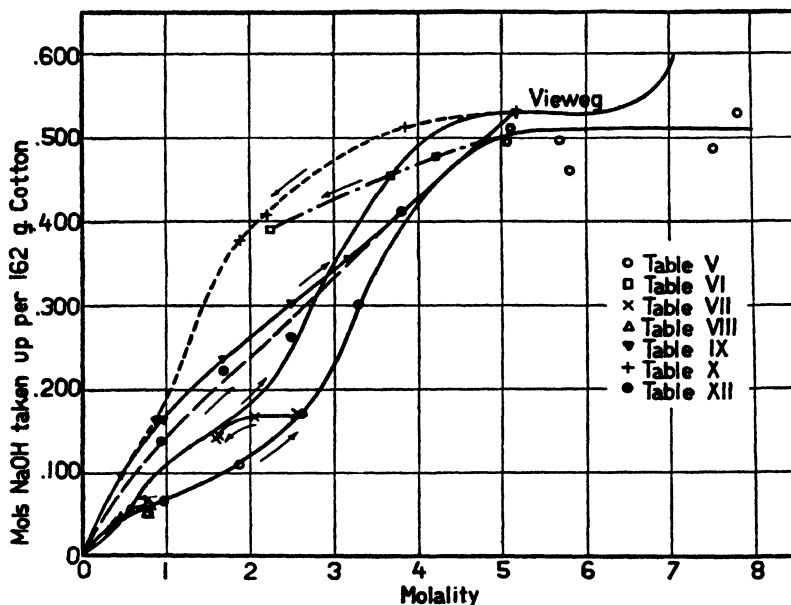


FIG. 2. Sodium hydroxide taken up by change-in-titer method

TABLE 3

Effect of caustic solution upon cotton pretreated with 14.4 per cent sodium hydroxide

CONCENTRATION OF NaOH	RESULTING X-RAY PATTERN
<i>per cent</i>	
2.68	Mercerized
5.99	Mercerized
8.38	Mercerized
10.8	Mercerized and Na-Cell I
11.85	Na-Cell I

Heuser has considered (7) that because the change-in-titer method gives higher values for the sodium hydroxide taken up the alkali cellulose compound should be formed at lower concentrations; he has predicted that the change in the x-ray pattern should result at a lower concentration in aqueous-alcoholic sodium hydroxide solution than in pure water. We have already shown that the true sorption values are many per cent higher than the change-in-titer values (1), and are nearer those from alcoholic

solution given above than the change-in-titer values. Furthermore, as shown above, the x-ray pattern of the cellulose does not change when placed in alcoholic caustic soda where the amount taken up is in excess of that of the compound which Heuser holds exists.

Hess and Trogus (5) have obtained some very interesting results with methanol solutions of sodium hydroxide. They found that when ramie fibers are treated with water-free 20 per cent sodium hydroxide-methanol solution for one day there is no change in the x-ray pattern. However, if the fibers are steeped in this liquor for more than a week, the cellulose interferences disappear gradually and the fiber diagram of Na-Cell III or Na-Cell II is obtained. While the experimental data are not at hand, we would expect some swelling of the fibers in sodium hydroxide-methanol solutions, but not as much as in water. Kress and Bialkowsky (8) have shown that water is a better swelling agent for cellulose than alcohol, so that the rôle of the solvent appears to be an "opening wedge" for the penetration of the caustic, although water must be part of the compound Na-Cell I, as the

TABLE 4

Effect of sodium hydroxide solution upon ramie pretreated in 15.48 per cent sodium hydroxide

CONCENTRATION OF NaOH	RESULTING X-RAY PATTERN
<i>per cent</i>	
0.9	Mercerized diagram; no Na-Cell III'
1.45	Mercerized diagram; no Na-Cell III'
2.38	Mercerized diagram; no Na-Cell III'
3.0	Mercerized diagram; no Na-Cell III'

drying of Na-Cell I causes the formation of Na-Cell III (5). However, it certainly appears that the greater the swelling the greater and quicker will be the penetration of the caustic into the lattice. In support of this position Hess and Trogus (5) have shown that unstretched ramie when treated with about 12.5 per cent caustic soda and then washed gives the caustic pretreated ("hydrate") diagram whereas, under unspecified tension, 30 to 35 per cent solution was necessary to obtain the new interferences. They have shown also (4) that ramie fibers under sufficient tension in 45 per cent caustic solution for more than a week gave the interferences of native cellulose when washed out under tension.

Hess and Trogus (5) emphasize that water is necessary for the formation of Na-Cell I and for rearrangement of Na-Cell II to Na-Cell I. If by adding water Na-Cell II changes to Na-Cell I, and the latter to "hydrate" cellulose, then one wonders what pattern would be obtained if native cellulose were treated for, say, two weeks with water-free 20 per cent sodium hydroxide-methanol, the caustic neutralized with dry hydrogen

chloride, and the sample then washed chloride-free with water. This would tell whether or not Na-Cell I is a necessary stage in the formation of "hydrate" cellulose.

HOW CAUSTIC SODA IS TAKEN UP BY CELLULOSE

If we apply the Phase Rule, using only temperature and concentration as independent variables, we have three explanations for the mechanism, i.e., formation of solid solution, adsorption of caustic soda, or the formation of sodium cellulosate. The first is ruled out as the diagram does not change continuously; the second possibility does not account for the change in diagram as the diffractions are not those of sodium hydroxide; the third does take care of the change in diagram.

Bancroft and Calkin pointed out previously (1) that data should be obtained on the taking up of caustic soda by precipitated cellulose. This would eliminate the possibility of the fibrous or "grown structure" being a

TABLE 5

Change-in-titer amount of caustic soda taken up by precipitated cellulose

MOLALITY OF FINAL SOLUTION	MILLIGRAMS OF SODIUM HYDROXIDE TAKEN UP PER GRAM OF CELLULOSE
0.399	25.7
0.775	37.3
1.660	61.1
2.600	78.7
3.590	110.9
5.030	118.0
8.470	121.7
12.30	169.0
6.250	118.5
9.690	161.0

variable. Some purified cotton was dissolved in cuprammonium solution, precipitated by extruding into sulfuric acid, and then given the usual 17.5 per cent α -cellulose treatment. Change-in-titer amount of caustic was then determined, the data being given in table 5 and in figure 3. It is evident in figure 3 that the curve is smooth up to 8 molal sodium hydroxide, beyond which the caustic is probably attacking the cellulose. The curve does not necessarily coincide with the previous curves, because the cellulose is modified as one precipitates it.

The main point to bear in mind is that the fibrous form or "grown structure" of cotton is not a variable so far as the Phase Rule is concerned.

Eisenschitz (3) has shown that with the introduction of a membrane, the concentration and temperature may be varied without violating the Phase Rule. This is simply adding another independent variable, so that

$$F = C - P + 3$$

On this basis Hess (6) has considered that two solid phases (cellulose and sodium cellulosate) are present. We prefer to consider that there is only one solid phase consisting of sodium cellulosate adsorbed on cellulose.

Referring to figure 1, it will be seen that Na-Cell I is formed where two moles of sodium hydroxide are taken up per mole of cellulose. The compound contains water, but progressive dehydrations have not been made, so that it is not possible to say whether the maximum water is necessary.

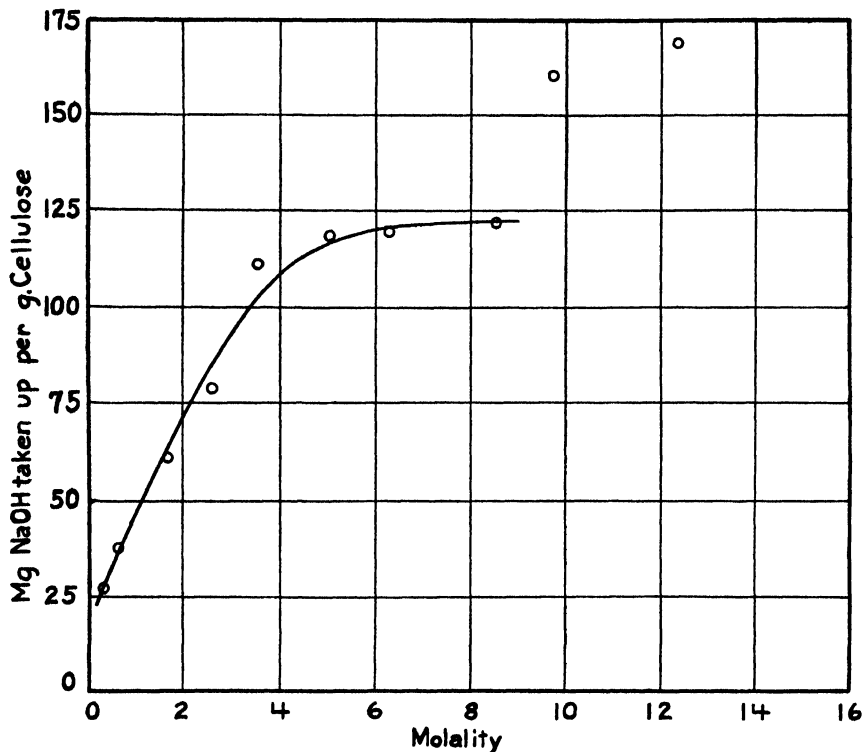


FIG. 3. Sodium hydroxide taken up by regenerated cellulose (change-in-titer method)

Scherer has shown (8a) that when cellulose is placed in liquid ammonia and sodium is added hydrogen is given off. An x-ray analysis of this system may shed light on the composition of the compound.

SUMMARY

1. The x-ray data have been correlated with our previous adsorption values for cotton.
2. It has been shown that cotton treated with sodium hydroxide in ethyl alcohol solution does not form mercerized cotton.
3. Pretreated cotton forms Na-Cell I at a lower concentration than native cotton.

4. It has not been possible to obtain Na-Cell III' under our experimental conditions.
5. A sodium cellulosate is formed which is adsorbed by the cellulose.
6. The use of the x-ray method to supplement adsorption curves is very important and could be used very profitably.

The writer wishes to acknowledge his indebtedness to Professor Bancroft, under whose direction this work was carried out, to the Textile Foundation for financial assistance, and to Professor Katz for his suggestions and the use of his x-ray equipment.

REFERENCES

- (1) BANCROFT AND CALKIN: J. Phys. Chem. **39**, 1 (1935).
- (2) BANCROFT AND CALKIN: Textile Res. **4**, 119 (1934).
- (3) EISENSCHITZ: Z. physik. Chem. **162A**, 216 (1932).
- (4) HESS AND TROGUS: Z. physik. Chem. **4**, 321 (1929).
- (5) HESS AND TROGUS: Z. physik. Chem. **11**, 381 (1930).
- (6) HESS, TROGUS, AND SCHWARZKOPF: Z. physik. Chem. **162A**, 187 (1932).
- (7) HEUSER: Cellulosechem. **8**, 31 (1927).
- (8) KRESS AND BIALKOWSKY: Paper Trade J. **93**, No. 20, 35 (Nov. 12, 1931).
- (8a) SCHERER AND HUSSEY: J. Am. Chem. Soc. **53**, 2344 (1931).
- (9) SCHWARZKOPF: Cellulosechem. **12**, 33 (1931).
- (10) SCHWARZKOPF: Z. Elektrochem. **38**, 353 (1932).
- (11) SUSICH AND WOLFF: Z. physik. Chem. **8**, 221 (1930).
- (12) TROGUS: Z. physik. Chem. **22B**, 134 (1933).

THE OXIDE FILM ON PASSIVE IRON¹

WILDER D. BANCROFT AND J. D. PORTER

Department of Chemistry, Cornell University, Ithaca, New York

Received June 20, 1935

Nowadays nearly everyone admits that there is an oxide film on the surface of passive iron, but there is still quite a difference of opinion as to the composition of the oxide. In England they incline to the belief that the film is ferric oxide, Fe_2O_3 . Evans (3) dissolved the iron from a piece of passive iron and obtained a residual film of ferric oxide. This proves nothing as to the initial composition of the oxide if one admits the possibility, suggested by Bennett and Burnham (2) in the Cornell laboratory, that the film is an instable oxide, stabilized by adsorption on iron. On removal of the iron, the hypothetically-unstable, higher oxide would revert at once to the stable ferric oxide.

Hedges (8) heated iron slowly in concentrated nitric acid, and found that at first the iron was passive and the solution almost colorless. At about 65°C. a faint yellow color appeared in the liquid, and at 75°C. a slow evolution of small bubbles of gas occurred at the surface of the metal. At higher temperatures the iron dissolved suddenly and with explosive violence. Powdered ferric oxide was ignited in a silica crucible, cooled in a desiccator, and then placed in a test-tube containing 10 cc. of nitric acid (sp. gr. 1.42). At the ordinary temperature no coloration was produced in the acid and only the faintest yellow was formed when the ferric oxide was left for twenty-four hours at 30°C. The rate of solution of ferric oxide in nitric acid under these conditions is therefore roughly comparable with that of passive iron.

"When the temperature was raised slowly, as in the experiments on the transition of passive iron, the first faint yellow color was produced at 68°; at 75° the solution rapidly became deep yellow, and the thin deposits on the sides of the bottom of the tube vanished between 75° and 77°. The heating was continued up to 90° without further change other than a general deepening of the yellow color. The total amount of ferric oxide dissolved was small. In an experiment carried out in 90 per cent nitric acid, the first faint yellow color appeared at 64°, and the solution became deep yellow over the range of 72° to 77°. It appears, therefore, that the tempera-

¹ Presented at the Twelfth Colloid Symposium, held at Ithaca, New York, June 20-22, 1935.

ture at which passive iron becomes active in nitric acid coincides with that at which the rate of solution of ferric oxide becomes appreciable."

This seems quite impressive, but really proves nothing, because the agreement is purely arbitrary and has no theoretical significance. We repeated Hedges' experiment, using ferric oxide which had been sintered at 1000°C. for half an hour. It did not dissolve even in boiling concentrated nitric acid. When the oxide was merely dried at 150°C., it dissolved at room temperature. Hedges happened to give his oxide just the right heat treatment to make the experiment a misleading one.

Bennett and Burnham (2) showed that iron could be made passive by dipping it into a potassium ferrate solution. This proved that the adsorbed oxide film could not be a higher oxide than FeO_3 , but did not exclude the possibility of the film being Fe_2O_5 or Fe_2O_4 . Actually there were data in the literature by Haber (4) and by Haber and Pick (6) which permit the fixing of a lower limit.

They say that "when wrought iron (sheet, polished with emery) and file-steel are made anodes (at 29° or 22°, respectively) in a caustic potash solution of specific gravity 1.36 (measured at 26°) with a current density of several amperes per square decimeter, red streaks are formed during the first few moments after the circuit has been closed. After several seconds the only anode reaction observed is the evolution of oxygen. This transient formation of ferrate can, however, be produced as often as desired, merely by reversing the current, making the original anode cathode for a moment, and then making it anode again."

We found this experiment easy to repeat, using a strip of Armco ingot iron and an anode current density of about ten amperes per square decimeter. With this current density red streamers of ferrate solution are at first carried away from the anode by the rising bubbles of oxygen. After a few seconds the formation of ferrate ceases, the anode having become completely passive. If we use a much lower current density, ferrate and oxygen continue indefinitely to be formed simultaneously, though in varying relative proportions. When the current density is increased, the formation of ferrate decreases and finally stops altogether, at least so far as visual tests are concerned.

Since the formation of ferrate occurs at a lower current density than the going passive, the oxide film on passive iron in these solutions cannot be a lower oxide than FeO_3 . The situation is, therefore, that Haber and Pick (6) have proved that the film producing passivity is not a lower oxide than FeO_3 , while Bennett and Burnham (2) have proved that it is not a higher oxide than FeO_3 . Consequently the oxide film in these solutions has the composition FeO_3 , is an instable oxide, and is stabilized by adsorption on iron, just as the free color-base of rosaniline is stabilized by adsorption on silk (Bancroft (1)).

These experiments prove nothing as to the composition of the oxide film in acid solution. As a matter of fact, we rather hoped that the oxide film would be FeO_3 in nitric acid and FeO_2 or Fe_2O_4 in hydrogen peroxide, but we had no such luck as that. We were able, however, to identify the oxide films obtained in other ways by making electromotive force measurements.

Heathcote (7) showed that nitric acid of sp. gr. 1.20 will not make iron passive, but will keep passivated iron passive for a considerable time. Hence we can passivate iron with any desired passivating agent, dip it into nitric acid (sp. gr. 1.20), and then measure the electrical potential against a normal calomel electrode. The calomel electrode is always anode to passive iron.

The intrinsic instability of the passive film and the fact that adsorption is involved make passive iron potentials difficult to reproduce. The observed potential is a function of time, and of the area, previous history, and conditions of immersion of the sample. If we make a piece of iron passive, measure its potential, make it active again, and repeat, we do not always obtain the same potential. When we try to compare different samples of iron and different passivating agents, annoyingly large variations in potential occur, but valid comparisons are possible if a large number of trials is made.

We are justified in taking the most noble of a series of potential readings as the nearest to the true value for the oxide film. The occurrence of weak spots or "active centers" in the film tends to lower the potential, as pointed out by Haber and Goldschmidt (5), while no conceivable circumstances can cause too high a potential. For these measurements we used lengths of Baker's No. 30 iron wire "for analysis" ($\text{Fe} = 99.8$ per cent) sealed into glass with 1 cm. projecting, giving an exposed area of about 0.08 cm.^2 When the potential of such an electrode was being measured, the exposed iron surface was immersed completely in the nitric acid (sp. gr. 1.20) in order to avoid an air-liquid-iron junction, at which activation is known to be rapid. Potentials were measured against a normal calomel electrode, using a Leeds and Northrup potentiometer, student type. Table 1 gives typical values of the potential of iron made passive by various means.

Electrode No. 1 was first made passive in nitric acid of specific gravity 1.42, then transferred to nitric acid of specific gravity 1.20 and its potential measured with reference to the normal calomel electrode. The highest value obtained was $+0.752$ volt with the iron electrode as cathode. After activation in hydrochloric acid, the electrode was made anode in a potassium hydroxide solution of specific gravity 1.36 and polarized with a current of 10 to 15 milliamperes. After this treatment the potential in nitric acid of specific gravity 1.20 was $+0.746$ volt. The iron wire was reactivated and then made passive by dipping for several minutes in a potassium fer-

rate solution prepared from iron and potassium nitrate as described by Bennett and Burnham (2). The highest potential this time was +0.741 volt. As a check, the wire was again made passive in concentrated nitric acid, after which it gave a potential of +0.741 volt. The difference between this and the initial value of +0.752 volt is probably due to changes in the surface during the several activations and deactivations.

These potentials lie so near together that iron, made passive by potassium ferrate, by anodic polarization in alkali, and by concentrated nitric

TABLE 1
Potentials of passive iron in nitric acid (sp. gr. 1.20)
The normal calomel electrode is always anode

ELEC- TRODE	PASSIVATING AGENT	MAXIMUM E_c
		volts
No. 1	HNO ₃ , sp. gr. 1.42	+0.752
	Anodic polarization in KOH, sp. gr. 1.36	0.746
	K ₂ FeO ₄ solution	0.741
	HNO ₃ , sp. gr. 1.42	0.741
No. 2	30 per cent H ₂ O ₂ (superoxol)	0.754
	HNO ₃ , sp. gr. 1.42	0.753
	8 per cent CrO ₃ in water	0.754
	2 per cent CrO ₃ in water	0.749
No. 3	HNO ₃ , sp. gr. 1.42	0.740
	KMnO ₄ solution, 1.7 N (0.3 N in H ₂ SO ₄)	0.734
No. 4	HNO ₃ , sp. gr. 1.42	0.743
	15 cc. HNO ₃ + 0.5 cc. H ₂ O	0.751
	15 cc. HNO ₃ + 1.0 cc. H ₂ O	0.752
	15 cc. HNO ₃ + 1.5 cc. H ₂ O	0.753
	15 cc. HNO ₃ + 2.0 cc. H ₂ O	0.753
	15 cc. HNO ₃ + 2.5 cc. H ₂ O	0.754
	15 cc. HNO ₃ + 4.0 cc. H ₂ O	0.755
	15 cc. HNO ₃ + 5.0 cc. H ₂ O (= sp. gr. 1.35)	0.742
	HNO ₃ , sp. gr. 1.42	0.739

acid, must be protected by the same oxide. Since this oxide cannot be either higher or lower than FeO₃, it must be FeO₃.

Electrode No. 2 was made passive successively in 30 per cent hydrogen peroxide, in concentrated nitric acid, and in an 8 per cent and a 2 per cent solution of chromium trioxide in water. The maximum potential attained in each of these cases, measured as before in nitric acid of specific gravity 1.20, lay between +0.749 volt and +0.754 volt with the iron electrode as cathode. This confirms the belief that the passivity produced by all these reagents is due to the formation of the same oxide, FeO₃.

A third electrode was made passive in concentrated nitric acid and then in an acidified potassium permanganate solution. Maximum potentials of +0.740 volt and +0.734 volt were obtained, which are sufficiently close to prove that the passivity produced by acid permanganate is due to the formation of FeO_3 .

Electrode No. 4 was made passive successively in six concentrations of nitric acid lying between specific gravities 1.42 and 1.35. In each case the maximum potential lay between +0.742 volt and +0.755 volt, thus proving that the same oxide, FeO_3 , is formed by all nitric acid solutions concentrated enough to produce passivity.

Bennett and Burnham (2) emphasized the part played by adsorption in stabilizing the oxide film. If the higher oxide is really adsorbed on the iron, the potential should vary continuously between certain limits. Lest this conclusion would seem to be belied by the relatively consistent potentials given in table 1, we mention again that only the highest, relatively stable values of the potentials have been included in the table. Since these correspond to a practically complete covering of the surface by a maximum thickness of oxide, the data agree fairly well among themselves. Dozens of values between +0.4 volt and 0.7 volt were obtained, especially when the attempt was made to use strips of iron instead of wires. Although these potentials are of no use for comparative purposes, they do indicate that adsorption is playing a part. Since a film of FeO_3 which covers only part of the surface tends either to repair itself or to break down completely, a determination of an adsorption isotherm is out of the question.

While Murphy was studying the oxidizing and reducing action of hydrogen peroxide, he came across a beautiful instance of the misleading experiment. As everybody knows, dilute hydrogen peroxide makes passive iron active. Murphy found that concentrated hydrogen peroxide makes passive iron active. This looked as though concentrated hydrogen peroxide was acting as a reducing agent, but it proved not to be true. Hydrogen peroxide is decomposed catalytically at the surface of passive iron. With concentrated hydrogen peroxide the amount decomposed per unit time is so great that the heat evolved raises the temperature to a point at which FeO_3 breaks down. It is as simple as that, but it had us guessing for a while.

In this paper we have shown that:

1. The evidence brought forward by Evans and by Hedges to show that the film on passive iron is Fe_2O_3 does not prove anything in regard to this.
2. The film making iron passive and produced by adsorption from a ferrate solution, $\text{K}_2\text{O} \cdot \text{FeO}_3$, is an oxide no higher than FeO_3 (Bennett and Burnham).
3. The film making iron passive and produced by anodic polarization of iron in a concentrated solution of potassium hydroxide is an oxide no lower than FeO_3 (Haber).

4. Since the two films are the same, the composition must be FeO_3 (Bancroft and Porter).

5. Electromotive force measurements in nitric acid of specific gravity 1.20 prove that the same film of FeO_3 is formed when iron is made passive by adsorption from an alkaline ferrate solution, by anodic polarization in alkali, or by treatment with hydrogen peroxide, chromic acid, acid potassium permanganate, or nitric acid of specific gravities between 1.35 and 1.42.

6. The activation of passive iron by concentrated hydrogen peroxide is the result of heating and not of reduction.

REFERENCES

- (1) BANCROFT: Applied Colloid Chemistry, p. 147 (1932).
- (2) BENNETT AND BURNHAM: Trans. Am. Electrochem. Soc. **29**, 217 (1916).
- (3) EVANS: J. Chem. Soc. **1927**, 1020; **1929**, 2651.
- (4) HABER: Z. Elektrochem. **7**, 216 (1900).
- (5) HABER AND GOLDSCHMIDT: Z. Elektrochem. **12**, 62 (1906).
- (6) HABER AND PICK: Z. Elektrochem. **7**, 713 (1901).
- (7) HEATHCOTE: J. Soc. Chem. Ind. **26**, 899 (1907).
- (8) HEDGES: Protective Films on Metals, pp. 102-4 (1932).

THE PHASE RULE IN COLLOID CHEMISTRY¹

WILDER D. BANCROFT

Department of Chemistry, Cornell University, Ithaca, New York

Received June 20, 1935

Gibbs pointed out that the phase rule does not apply, in the form in which he deduced it, to systems involving surface forces, in other words to colloids. On the other hand we make use of the phase rule, consciously or unconsciously, every time that we determine an adsorption isotherm. We have made use of the theorem consciously when studying the action of acids and bases on proteins and on cellulose. What postulates must we make in order to justify our application of the phase rule?

In the first place we must be dealing with reversible equilibrium because the phase rule applies only to reversible equilibrium. In the early days of colloid chemistry, people were interested chiefly in irreversible reactions and metastable states; but that is no longer true.

When dealing with reversible equilibrium in systems containing colloids, it will be profitable to consider separately the adsorbent and the adsorbed substance. Since adsorption depends on the shape and structure of the adsorbing material as well as on its chemical nature, one gram of charcoal may contain a hundred, a thousand, ten thousand, or more solid phases. That seems like a hopeless situation, but it is not really bad. Two different 1-g. lots of charcoal will not necessarily behave alike, but each lot will act like a single phase so long as the individual grains do not change. When we study the adsorption of hydrogen by platinum black, and get an entirely different result after evacuating the hydrogen once or twice, we recognize that the platinum black has sintered and changed its structure. Consequently we put the platinum on an asbestos substrate and get approximately reproducible results because the platinum does not sinter. We see, therefore, that each separate lot of an adsorbent will act as a single solid phase so long as the individual particles are unchanged, but that two separate lots of the same adsorbent will not necessarily act like the same solid phase. With this limitation the phase rule holds for all adsorbents.

When we come to the substance that is to be adsorbed or peptized, we make the explicit assumption that, from the viewpoint of the phase rule, an adsorbed film or a peptized substance shall not be considered as a sepa-

¹ Presented at the Twelfth Colloid Symposium, held at Ithaca, New York, June 20-22, 1935.

rate phase even though we know that it is. On this basis, charcoal and a gas which is adsorbed by it constitute a two-component, two-phase system. At constant temperature there is only one amount of adsorption for each pressure and the adsorption isotherm is perfectly definite, so long as the solid phase does not change. The adsorption of caustic soda from aqueous solution by cellulose comes under the phase rule so long as the cellulose does not change.

If we consider a substance peptized by water as not constituting another phase from the viewpoint of the phase rule, the liquid with the suspended particles becomes a phase of varying composition and can be treated as a solution so long as the degree of dispersion remains constant. This enables us to account for the mordanting of cotton with tannin or for the dyeing of cotton by substantive dyes.

We bear up bravely over light being considered either as particles or as waves, depending on the nature of the experiment. If, however, there are any people who do not like to consider a peptized particle or an adsorbed film as being simultaneously both a separate phase and not a separate phase, it is always possible to avoid this by saying that you have a new phase of such a nature that it introduces an extra degree of freedom. Everything can be accounted for on that basis without postulating a dualistic behavior of an adsorbed film or a peptized substance. That has been suggested by a number of people, but it has never proved satisfactory and is therefore objectionable from a pragmatic point of view.

When we study the action of aqueous caustic soda on cellulose from the phase-rule point of view, we get apparently one set of results, and when we study the same system from the x-ray point of view, we get apparently a different set of results. The x-ray people say that their method is the best and that consequently their results are the only ones worth considering. That is foolish, and the two sets of results must somehow be made to agree. There is no question but that the x-ray pattern of cellulose changes irreversibly when treated with a caustic soda solution containing 13 per cent or more of caustic soda. This shows on the adsorption isotherm in a change of direction and in a new set of values at lower concentrations. There is, however, no evidence of two solid phases, although mixed x-ray diagrams can be obtained. The discrepancy disappears if we postulate that each modification of cellulose adsorbs the other and that an adsorbed substance can give an x-ray diagram. The x-ray people have always assumed that a mixed diagram necessarily means two solid phases, but there is no experimental evidence in favor of this contention. The assumption rests on two other explicit assumptions, that the adsorption layer is only one molecule thick and that a layer one molecule thick cannot give an x-ray pattern.

If we eliminate the change in the x-ray pattern of cellulose by starting with mercerized cotton, we find a smooth adsorption curve with no sign of two solid phases. On the other hand an x-ray study of cellulose with caustic soda in it shows clearly the existence of at least two sodium cellulose-

sates which are definite chemical compounds. We must remember that the phase rule does not show in what form caustic soda is taken up by cellulose. It merely shows the number of solid phases present at any moment. In the absence of any other evidence we adopt the simplest form of statement and say that caustic soda is adsorbed by cellulose.

The discrepancy between the two methods of study disappears if we recognize that the phase-rule method shows the number of solid phases and does not show the form in which the dissolved or peptized substance is adsorbed, whereas the x-ray method shows the form in which the adsorbed substance is taken up but does not at present give any evidence as to the number of solid phases. The two methods are complementary and not contradictory.

From the combination of the two methods we can say absolutely that mercerized cotton adsorbs caustic soda as such from dilute solutions, one definite sodium cellulosate from stronger solutions, and another definite sodium cellulosate from still stronger solutions without there being at any time two solid phases present.

The general results of this paper are as follows:—

1. The phase rule can be applied in its ordinary form to reversible equilibrium in colloidal systems provided we remember that a solid adsorbent can be treated as a single solid phase only so long as the number and structure of the individual grains remain unchanged, and provided we treat an adsorbed substance or film and a peptized substance as not constituting new phases in the application of the phase rule, though they do constitute new phases in fact.

2. There are other ways of getting around the difficulty of treating a peptized substance as being simultaneously another phase and not another phase, but the other methods have not recommended themselves to chemists and are therefore unsatisfactory pragmatically.

3. The two modifications of cellulose adsorb each other and do not at any time occur as two solid phases.

4. If one admits that a mixed x-ray diagram does not necessarily connote two solid phases, the apparent discrepancies between the phase-rule method of study and the x-ray method of study disappear.

5. The phase-rule method of study shows the number of solid phases, but does not show the form in which an adsorbed substance is taken up.

6. The x-ray method of study shows, or may show, the form in which an adsorbed substance is taken up, but it does not necessarily show at present how many solid phases coexist.

7. The phase-rule and the x-ray methods of study of the system cellulose, caustic soda, and water are complementary and not contradictory.

8. From a dilute caustic soda solution, mercerized cellulose adsorbs caustic soda as such; from a more concentrated solution one sodium cellulosate is adsorbed; from a still more concentrated solution another sodium cellulosate is adsorbed. In none of these cases do two solid phases coexist.

BÖHMITE AND BAYERITE

H. LEHL

Received November 15, 1934

An article by Weiser and Milligan (31), entitled "X-ray Studies on the Hydrous Oxides. I. Alumina," appeared in this Journal in December, 1932; from the x-ray photographs of preparations made in various ways the authors arrived at the following conclusions: "... there are two alumina hydrates: (1) gibbsite, $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, both natural and artificial, and (2) diasporic, $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$. Precipitated alumina aged at 100° has been found by x-ray diffraction methods to be a new form of alumina which has been termed $\delta\text{-Al}_2\text{O}_3$, with adsorbed water." In reply to this article Edwards and Tosterud (8) refer to the existence of an $\alpha\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ which differed from diasporic (to which they gave the designation $\beta\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$; cf. in what follows the designation of Haber (18)). Furthermore there was described a $\beta\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, which differed from gibbsite (hydrargillite, or $\alpha\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, according to Edwards and Tosterud).

The object of this communication is to draw attention to some publications which, although not mentioned by Weiser and Milligan or by Edwards and Tosterud, nevertheless bear on the matter. Proof will, moreover, be brought to show that the preparation which Weiser and Milligan termed "a mixture of $\delta\text{-Al}_2\text{O}_3$ and gibbsite" has likewise given a distinctive x-ray photograph, according to the radiograms by these authors, which belongs to a definite trihydrate, namely, bayerite, or β -trihydrate, according to Edwards and Tosterud (8).

BÖHMITE

Böhm and Niclassen (4), as well as Fricke and Wever (16), had already shown in 1924 that at higher temperatures (as, for instance, approximately $100^\circ\text{C}.$) aluminum hydroxide precipitated from a solution of aluminum sulfate with aqueous ammonia gave a hitherto unknown x-ray diagram. A year later Böhm published the reproduction of an x-ray photograph which showed the lattice of a very pure aluminum hydroxide having the composition $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ from Les Baux. This lattice of very definite form was different from those of diasporic, the trihydrate, and the oxide of aluminum, although the film shows the same lines as those which Böhm and Fricke had obtained from the preparations precipitated at a higher temperature.

The very pure bauxite mineral of Böhm was shown by a series of careful quantitative analyses to have the composition $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$. A preparation absolutely identical with this, both analytically and according to the radiogram, was made up by Böhm (3) from various aluminum hydroxide preparations in an autoclave with superheated steam at 200°C .; he then regarded it as pure bauxite and an "isomer of diaspore." Later, however, it was shown that it is not by any means invariably the case that the bauxite mineral found in nature contains this monohydrate as the predominating aluminum compound, as it may often contain diaspore, gibbsite, and others as well. (In this connection compare F. Rinne with Fricke and Wever (ref. 16, p. 322); see also de Lapparent (25) and the photographs of Weiser and Milligan (ref. 31, p. 3026)). Consequently, at the suggestion of de Lapparent, this isomer of diaspore discovered by Böhm was given the name of "bohmite;" this name has come to be widely adopted in European literature.

In order to avoid confusion, the nomenclature adopted in Europe has been made use of in connection with the subdivision of alumina into α -, β -, etc. forms. According to Haber (18) the aluminum hydroxides which, by elimination of water, give the cubic γ -oxide (2, 5) stable below 1000°C ., are termed γ -oxides; to this group belong böhmite, gibbsite, and bayerite, which will be described later (Tosterud designates these as $\alpha\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, $\alpha\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, and $\beta\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$). In contrast diaspore, which, when heated, gives hexagonal-rhombohedral α -corundum (19, 28) belongs, according to Haber, to the α -series (according to Tosterud, $\beta\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$).

The radiogram for "böhmite" given by Böhm is identical with the diagram of " $\delta\text{-Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ " published by Weiser and Milligan. According to its artificial representation it is, furthermore, identical with the preparations made and designated $\alpha\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ by Tosterud (30).

As has since been definitely ascertained by various observers, böhmite is the first product of aging aluminum hydroxide gel precipitated from solutions of aluminum salts with alkali. This is shown with great clearness by the work of Fricke and Meyring (14), who investigated the aging of aluminum hydroxide in alkaline media by determinations of solubility, pH measurements, and x-ray photographs, as also by the experiments, combined with x-ray photographs etc., conducted by Havestadt and Fricke (20) in regard to the dielectric constants of hydrous hydroxide suspensions depending on the state of aging. Kohlschütter and his collaborators (24) also found in the course of their extensive investigations into the aging of fresh gels that the formation of a crystallized trihydrate can never overtake the formation of the " β -gel" (a term used (24, 32) for a very slightly reactive gel which sometimes shows the x-ray lines of böhmite).

In all these investigations into the course of the aging of amorphous hydroxide, the x-ray diagram of böhmite was always obtained first, even

though it did not show (especially at the larger angles of deflection) the lines so clearly and sharply as those obtained from well-crystallized böhmite, which can be obtained from other aluminum hydroxide preparations of the Haber γ -series at 200–350°C. with undersaturated steam in an autoclave (3, 15, 22, 29, 30). Böhmite is also formed by slow thermal disintegration of the (γ)-trihydrate of aluminum oxide (1, 15). Well-crystallized böhmite is very stable and does not exhibit any noticeable signs of aging. At 405°C. böhmite remains undecomposed under a steam pressure of about 500 atmospheres, whereas diasporite under the same conditions breaks up into corundum and water (see ref. 15; this paper also includes some carefully obtained isobaric decomposition curves of böhmite and diasporite).

The density of a pure böhmite produced in an autoclave has been found by Fricke and Severin (15) to be $d_4^{20} = 3.014$. For a preparation likewise produced in an autoclave von Nieuwenburg and Pieters (27) found a figure of 3.06.

Coblentz (6) deduced from measurements of absorption in the infra-red that bauxite (as in the case of diasporite and gibbsite) is a true hydroxide (in this connection cf. Fricke and Severin, ref. 15, p. 298). The bauxite investigated by him, which had a composition of $\text{Al}_2\text{O} \cdot \text{OH}$, did not show any water bands. At 3μ , however, a band appeared which, from comparisons with other definite hydroxides, must be ascribed to the OH group. The formulation AlOOH is therefore to be preferred here, rather than $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$. (In regard to this, as well as other true hydroxides, cf. Fricke and Ackermann, ref. 12, p. 639.) According to Achenbach (1) böhmite is rhombic.

Weiser and Milligan also find the x-ray interference of böhmite in a series of their preparations. They ascribe these interferences, however, to a new oxide, " δ - Al_2O_3 ," which had adsorbed varying quantities of water. In proof of this, they state that the preparations having a water content of only 0.65 H_2O per 1 Al_2O_3 show the same radiogram as with a water content of more than 1 H_2O per 1 Al_2O_3 . This result is, however, not surprising; neither does it offer anything new in comparison with the findings of other authors, since the preparation with 0.65 H_2O per 1 Al_2O_3 must still contain up to 65 per cent of böhmite, and consequently must show its x-ray diagram. The diagram interference of the 35 per cent γ - Al_2O_3 need be only slightly visible, or even invisible altogether, as the γ -oxide obtained by careful extraction of water from böhmite either reveals only a few, weak and widely-spaced, lines at a small angle of deflection, or even appears quite amorphous from a röntgenographic point of view (ref. 23, p. 328; also ref. 15, p. 301). The assumption of a " δ - Al_2O_3 " cannot therefore be deduced from the results of Weiser and Milligan.

BAYERITE

Weiser and Milligan (31) made further preparations according to the directions of Hüttig and Kostelitz (21), and from the x-ray photographs obtained from these preparations they arrived at the conclusion that, in the case of the preparations K_1' , K_1'' , K_2 , K_3 , and L_3 , according to Hüttig, there was no definite compound, but a mixture of $\delta\text{-Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ and gibbsite. In contrast, Hüttig and his collaborators (21, 23) ascribe these preparations to the "isomers of hydrargillite" first discovered by Böhm (3) and later carefully investigated by Fricke (9, 10, 11), which, in accordance with a proposal made by Fricke (9), because of the precipitation of the substance when alumina is prepared by K. J. Bayer's process, is now termed bayerite in European literature. This bayerite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$), to the properties of which we shall refer later, also belongs to the γ -series of Haber, since it produces cubic γ -oxide on complete extraction of water. It is metastable at room temperature in contrast to gibbsite (hydrargillite) (9, 10, 11, 17), but stable in comparison with böhmite (3, 20, 24). It is probably identical with the substance designated as $\beta\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ by Edwards and Tosterud.

It is quite evident from the photographs of Weiser and Milligan that their preparations, made "according to Hüttig," cannot be mixtures of böhmite and gibbsite; this may also be seen from a comparison of the positions of the lines of the alleged " $\delta\text{-Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ " (böhmite) and of gibbsite with the positions of the lines of the preparations according to Hüttig. To illustrate this fact table 1 has been compiled from data given by Weiser and Milligan (31).

Some of the special features which show that the preparations made according to Hüttig's method cannot be mixtures of böhmite (" $\delta\text{-Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ ") and gibbsite, are the following: (1) The strongest böhmite line ($D = 1.85$, $I = 10$) is exactly the one missing in the case of preparation K_3 , and therefore weaker lines could not be expected to appear. (2) The strongest gibbsite line ($D = 4.85$, $I = 10$) is likewise missing in K_3 . (3) Two of the three strongest lines of K_3 ($D = 4.79$, $I = 10$ and $D = 2.22$, $I = 10$) are not found in either böhmite or gibbsite.

The intervals between the lines just mentioned and adjacent lines in the different photographs are so great (at least 0.04 A. U.) that the findings given under sections (1) to (3) cannot be due to experimental errors. An arbitrary parallel displacement of the original film also does not permit of any position being found which would justify the interpretation of the preparations "according to Hüttig" as mixtures of böhmite and gibbsite. The preparations of Weiser and Milligan (31) are therefore, from a röntgenographic point of view, also bayerite, or the β -trihydrate of Edwards and Tosterud (8), which they have already indicated. The decomposition curves of Hüttig and Kostelitz (21) show, nevertheless, that their prepara-

tions consisted for the greater part of the "γ-gel" identified by Kohlschütter and his collaborators (24) as mixtures of "β-gel" and bayerite. ("β-gel" and "γ-gel" are used in the meaning given by Willstätter, Kraut, and col-

TABLE 1
Comparison of positions of lines
 $D = d_{hkl}/n$ in A.U.; I = relative intensity

$\delta\text{-Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ PHOTO DII (BÖHMITE)		GIBBSITE MINERAL		PREPARATION ACCORDING TO HÜTTIG, PHOTO KI (BAYERITE)	
D	I	D	I	D	I
3 16	5	4 85	10	4 79	10
		4 34	9	4 34	10
		3 31	1		
				3 19	4
		3 12	1		
		2 45	7	2 47	2
2 33	7	2 38	7	2 37	3
		2 66	1		
				2 26	1
				2 22	10
		2 17	3		
		2 04	3		
1 85	10	1.990	2	2 00	2
		1 907	2		
				1 89	1
		1 798	3		
		1 741	4	1 77	1
		1 681	5	1 72	7
1 43	8	1 642	0 1	1 65	1
		1 580	1	1 60	1
				1 55	2
		1 448	4	1 44	3
		1 404	6		
				1 39	3
1 32	5	1 352	2		
		1 312	1	1 33	4
1 13	1			1 21	2

laborators (32).) Most of the β-gels exhibit, however, either no interferences, or else very weak and diffuse böhmite interferences.

With regard to bayerite, reference may be made to the following litera-

ture. Böhm (3) discovered a trihydrate of Al_2O_3 which exhibited a very beautiful and characteristic radiogram totally different from that of gibbsite. A reproduction of the picture obtained with iron radiation of this crystal, known generally now as bayerite, may be found in Böhm's article. The angles for a pure bayerite for copper radiation are given by Fricke (10).

Bayerite is produced from böhmite gel ("β-gel" and fresh böhmite) by aging, production being slow under cold water (3, 20, 24), but rapid under dilute alkali (10, 14). In an intermediate stage of the aging, according to Kohlschütter and collaborators (24), "somatoids" form from minute needles of bayerite, which are either wholly or partly surrounded by β-gel (böhmite gel). (Microphotographs of these somatoids may be seen in the paper of Kohlschütter and collaborators (24). Willstätter, Kraut, and Erbacher (32) term these somatoids "γ-gels." Under certain conditions these "γ-gels" can have such a composition that various authors were thereby led to believe that they had found a dihydrate of Al_2O_3 .)

Long and extensive shaking with not too dilute alkali, best at a rather high temperature (50–60°C.), causes bayerite to change into gibbsite (hydrargillite) (9). The series order of stability is therefore böhmite > bayerite > gibbsite.

According to the procedure followed, various forms of aluminum hydroxide can be obtained from an alkali-aluminate solution. The rapid introduction of carbon dioxide into a dilute aluminate solution gives röntgenographically amorphous aluminum hydroxide (ref. 20, p. 379; ref. 9). On the contrary, if carbon dioxide be allowed to pass in slowly at ordinary temperatures, so that some days are required for complete precipitation, one obtains bayerite. The aluminate solution may also be more concentrated, for example, with a specific gravity of 1.15 (17). If the carbon dioxide be allowed to act very slowly at ordinary temperature, as, for instance, by allowing the container to stand exposed to the air, then gibbsite is obtained (9). Gibbsite of larger crystalline structure may be obtained more rapidly by allowing carbon dioxide to pass slowly over a solution of aluminate heated to 96–100°C. (1).

The same holds good for the spontaneous (hydrolytic) precipitation of the alumina hydrate from a solution of aluminate, which also takes place when air is excluded. Provided the temperature is the same, a slow precipitation is then favorable for the formation of gibbsite, and rapid precipitation for bayerite (9). More accurate details for the production of the two alumina hydrates in this manner, which is important from a technical point of view, may be found in other articles (11, 13, 17).

Apart from x-ray photographs which, in the case of good and well-crystallized preparations, reveal sharp lines up to the highest angles of deflection, the bayerite preparations of Fricke and his collaborators were also investigated, in part for physical uniformity, experiments being made to

discover whether the solubility in alkali remained constant with the quantity of excess undissolved solid, where the quantity of alkali was kept the same. If it were a case of a mixture of constituents of different solubilities, the solubility should increase. The results, however, showed a good degree of constancy in a number of cases (ref. 13 and unpublished work).

In the case of these tests care must be taken to see that the alkali used is not too concentrated, so that the sediment does not change into aluminate (see the solution equilibria in the article by Fricke and Jucaitis (13)).

Fricke and Wullhorst determined the heat of solution of bayerite and gibbsite in 12 per cent hydrofluoric acid. They found 37.8₄ and 36.5₉ kg-cal. per mole, respectively, that is, for bayerite an excess of heat content amounting to 1.2 kg-cal., which is quite in accord with the order of stability ascertained by conversion experiments.

Fricke and Severin (15) examined the isobaric thermal decomposition of bayerite, together with that of gibbsite, for vapor pressures of 100 mm. of mercury. In contrast to other earlier work, it was found in these experiments that the reaction spaces amounted in all to only 0.3 to 0.8 cc., of which two-thirds to four-fifths was filled with the hydroxide in a very fine powder. The time for pressure attainment amounted, nevertheless, to as much as sixty days. In this careful method a decomposition temperature of 120°C. was found for bayerite, and for gibbsite 165°C., both for equilibrium with böhmite (badly crystallized) produced by the decomposition. From Nernst's approximate equation it is possible to calculate from these results the heat of formation of bayerite from böhmite and 2H₂O (vapor) as 32.4 kg-cal., and for the corresponding heat of formation of gibbsite, 36.3 kg-cal. The figures are again in conformity with the order of stability, but are not capable of rigorous comparison on account of the certainly different energy content of the böhmite formed at the two vapor pressure equilibria as the second phase (12).

In the article by Fricke and Severin (15) there is also to be found an exhaustive discussion of the results of the thermal decomposition experiments of Hüttig and von Wittgenstein (23), of Hüttig and Kostelitz (21), and of other authors.

Finally, it should be pointed out that by investigations of structure conducted by Megaw (26) and Deflandre (7), gibbsite, bayerite, and diaspora are shown to be true hydroxides, in which the water is present not as such, but in the form of OH ions. (Note, also, what has been said previously in regard to absorption measurements in the infra-red.)

SUMMARY

Four definite crystallized forms of aluminum hydroxide are known, namely: diaspora $\left(\text{Al} \begin{array}{c} \diagup \text{O} \\ \diagdown \text{OH} \end{array} \right)$, which, by extraction of the water, gives

hexagonal-rhombohedral α -corundums, and three other forms, which, when water is extracted, give cubic γ - Al_2O_3 . These are, in order of increasing stability, böhmite $\left(\text{Al} \begin{smallmatrix} \nearrow \text{O} \\ \searrow \text{OH} \end{smallmatrix}\right)$, bayerite $(\text{Al}(\text{OH})_3)$, and gibbsite $(\text{Al}(\text{OH})_3)$.

REFERENCES

- (1) ACHENBACH, H.: Chem. Erde **6**, 307 (1931).
- (2) BELJANKIN, D., DILAKTORSKY, N., KRASNIKOW, A., AND KOWALEW, P.: Centr. Mineral. Geol. **A1932**, 242.
- (3) BÖHM, J.: Z. anorg. Chem. **149**, 203 (1925).
- (4) BÖHM, J., AND NICLASSEN, H.: Z. anorg. Chem. **132**, 5 (1924).
- (5) BRILL, R.: Z. Krist. **83A**, 325 (1932).
- (6) COBLENTZ, W. W.: Jahrb. Radioakt. Elektronik **3**, 397 (1906).
- (7) DEFLANDRE, M.: Bull. soc. mineral. **55**, 140 (1932).
- (8) EDWARDS, J. D., AND TOSTERUD, M.: J. Phys. Chem. **37**, 483 (1933).
- (9) FRICKE, R.: Z. anorg. Chem. **175**, 249 (1928).
- (10) FRICKE, R.: Z. anorg. Chem. **179**, 287 (1929).
- (11) FRICKE, R.: Kolloid-Z. **49**, 229 (1929).
- (12) FRICKE, R., AND ACKERMAN, P.: Z. Elektrochem. **40**, 630 (1934).
- (13) FRICKE, R., AND JUCAITIS, P.: Z. anorg. Chem. **191**, 129 (1930).
- (14) FRICKE, R., AND MEYRING, K.: Z. anorg. Chem. **214**, 269 (1933).
- (15) FRICKE, R., AND SEVERIN, H.: Z. anorg. Chem. **205**, 287 (1932).
- (16) FRICKE, R., AND WEVER, F.: Z. anorg. Chem. **136**, 321 (1924).
- (17) FRICKE, R., AND WULLHORST, B.: Z. anorg. Chem. **205**, 131 (1932).
- (18) HABER, F.: Naturwissenschaften **13**, 1007 (1925).
- (19) HARRINGTON, E. A.: Am. J. Sci. **13**, 467 (1927).
- (20) HAVESTADT, L., AND FRICKE, R.: Z. anorg. Chem. **188**, 357 (1930).
- (21) HÜTTIG, G. F., AND KOSTELITZ, O.: Z. anorg. Chem. **187**, 1 (1930).
- (22) HÜTTIG, G. F., AND SCHAUFEL, A.: Kolloid-Z. **55**, 199 (1931).
- (23) HÜTTIG, G. F., AND VON WITTGENSTEIN, E.: Z. anorg. Chem. **171**, 323 (1928).
- (24) KOHLSCHÜTTER, V., BERLIN, M., BEUTLER, W., AND SPRENGER, I.: Helv. Chim. Acta **14**, 3, 305 (1931).
- (25) LAPPARENT, J. DE: Compt. rend. **184**, 1661 (1927).
- (26) MEGAW, H. D.: Z. Krist. **87**, 185 (1934).
- (27) NIEUWENBURG, C. J. VON, AND PIETERS, H. A. J.: Rec. trav. chim. **48**, 27 (1929).
- (28) PAULING, L., AND HENDRICKS, S. B.: J. Am. Chem. Soc. **47**, 781 (1925).
- (29) SCHWIERSCH, H.: Chem. Erde **8**, 252 (1933).
- (30) TOSTERUD, M.: Canadian patent 285,147 (1928).
- (31) WEISER, H. B., AND MILLIGAN, W. O.: J. Phys. Chem. **36**, 3010 (1933).
- (32) WILLSTÄTTER, R., KRAUT, H., AND ERBACHER, O.: Ber. **58**, 2448 (1925).

THE DIFFUSION COEFFICIENT AND APPARENT RADIUS OF THE CUPRIC ION IN SILICA GELS

W. G. EVERSOLE AND EDW. W. DOUGHTY

Division of Physical Chemistry, The State University of Iowa, Iowa City, Iowa

Received September 1, 1934

In a recent paper (1) a mathematical basis has been presented for the calculation of diffusion coefficients from measurements of the rate of penetration of any constant concentration of a diffusing substance into a diffusion medium. The method requires simultaneous measurements of the distance of penetration and the time, and a constant concentration of diffusing substance at zero distance.

The purpose of the present paper is to report the results of measurements of the diffusion of cupric chloride into gels. The photometric method which was used permits making the measurements without disturbing the diffusion process in any way.

APPARATUS

The diffusion apparatus (figure 1) consisted essentially of a light source, a collimating device made up of a series of slits, a cell used as a container for the diffusion system, and a photoelectric cell which was connected to a suitable indicating device.

For a light source of constant intensity a 500-watt projection lamp was operated from a 100-volt storage battery. The bulb was surrounded by a cooling coil to prevent excessive heating, and a red gelatin light filter was placed between the light source and the first slit. The slit nearest the photoelectric cell consisted of two parallel plates 2.2 x 5 cm. The width of the slit system was adjusted to approximately 0.015 cm.

The diffusion cell was formed by clamping rectangular pieces of plate glass (7.5 x 25 cm.) on either side of a glass rod which had been bent into a U-shape and covered with rubber tubing. The cell was fitted into an upright stand so arranged that it could be moved up or down at will by means of a screw adjustment. Readings of the height of the cell were taken to 0.01 cm. by means of a cathetometer.

The photoelectric cell was connected to a vacuum tube amplifier (figure 2). By means of the potentiometer and variable resistance shown in the diagram, it was possible to adjust the plate current of the vacuum tube to any suitable value for normal light intensity on the photoelectric

cell. Any change in light intensity was then indicated by a corresponding change in the plate current. The plate current was measured in arbitrary units by a millivoltmeter which gave full scale deflection with a current of approximately 20 microamperes.

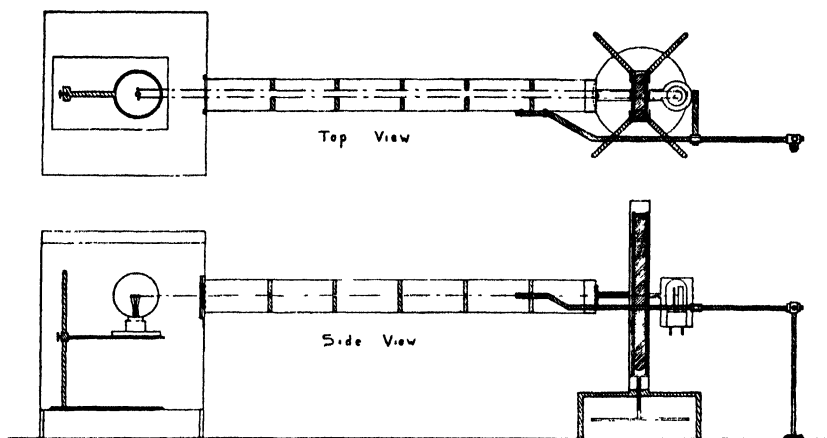


FIG. 1. Diagram of the diffusion apparatus

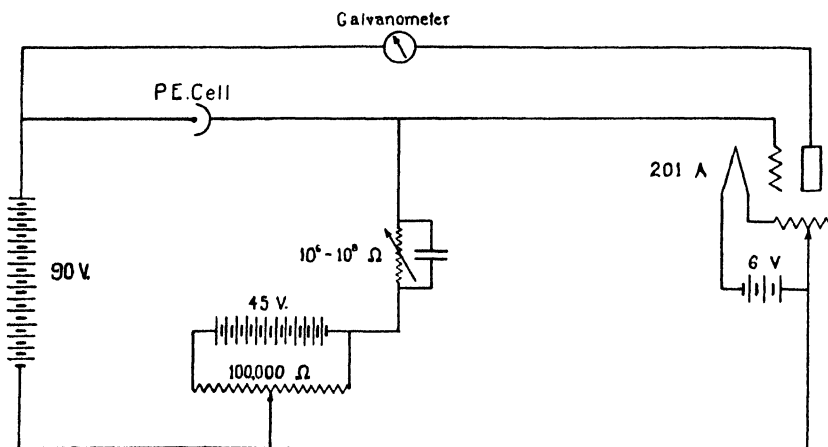


FIG. 2. Wiring diagram of amplifier

Except for narrow slits to permit passage of the light beam, both the light source and the photoelectric cell were enclosed in light-tight metal housings. The experimental work was carried out in a darkened room at $25 \pm 2^\circ\text{C}$.

EXPERIMENTAL METHOD

The sodium silicate (sp. gr. 1.160) which was used in making the gels was 1.59 *N*, as determined by titration with standard acid using methyl orange as indicator. The gels were made by addition of the sodium silicate solution to an equal volume of 4.752 *N* hydrochloric acid. The formation of clear gels required vigorous stirring of the mixture as the silicate was added. When more dilute gels were desired, water was added to the acid before the addition of the sodium silicate.

After the diffusion cell had been placed in the apparatus and a zero reading had been taken corresponding to the position of the cell when the light beam was coincident with the surface of the gel, the diffusing solution was poured on top of the gel. The concentration of the diffusing solution was kept constant throughout the measurement by continuous addition of fresh solution as the less dense solution was drawn off at the top by suction. In making the measurements, the cell was moved upward until further motion resulted in no further increase in the plate current of the amplifier. From this position the cell was moved slowly downward until the light beam passed through a portion of the gel containing cupric ions in the amount necessary to cause a 1 per cent decrease in the plate current. When this point was reached, a reading of the height of the cell was again taken. The distance (X_a) which that particular concentration ($m' = 6.65 \times 10^{-5}$ moles per liter) had moved downward at that time (t) was determined by the difference between this reading and the zero reading.

The most satisfactory results were obtained from one to twenty-four hours after the beginning of the diffusion process. During most of the first hour, the diffusion was too rapid for accurate measurement, and after a day or more there was evidence in some cases of a slight cracking (2) of the gel structure.

The value of the diffusion potential was estimated by measuring the potential difference between a saturated calomel electrode placed in the diffusing solution and a silver-silver chloride electrode placed in the gel. The difference between the voltage obtained using a saturated potassium chloride bridge and that obtained when the diffusing solution and the gel were in direct contact was taken as the diffusion potential. These values are small, as would be expected for systems of uniformly high electrical conductivity throughout.

CALCULATIONS AND RESULTS

Table 1 gives a summary of the values obtained from the diffusion measurements. The values of X_a^2/t were determined from the slope of the straight line obtained by plotting the values of X_a^2 against the values of t . In general the results of duplicate experiments agreed to within 0.1 per cent.

The values of the diffusion coefficient of the cupric ion were calculated by means of the equation

$$D = \frac{X_a^2}{4t} \left(1 - \frac{2UE}{X_a^2/t} \right)^2 \frac{1}{\ln m_0 - \ln m'} \quad (1)$$

In this equation m_0 is the concentration of diffusing substance at zero distance, m' is some constant concentration much lower than m_0 , and X_a is the distance of the concentration m' from the surface of the gel at time t . U is the mobility of the diffusing ion and is given the sign of the charge on the ion. E is the potential of the solution referred to that of the gel. U for the cupric ion was given a value of 4×10^{-4} cm. per second, which is approximately 0.7 of the value at infinite dilution. While this is an

TABLE 1
The diffusion coefficient and apparent radius of the cupric ion in silica gels

SiO ₂ PER LITER OF GEL	DIFFUSING SOLUTION		$X_a^2/t \times 10^4$	E	$D \times 10^6$	$r \times 10^8$
	CuCl ₂ (m_0)	Added electrolyte				
grams	moles per liter	moles per liter	cm ² . per second	mv	cm ² . per second	cm
104.6	0.5	0.795 NaCl 1.58 HCl	1.233	-3.0	3.59	6.75
104.6	1.0	1.58 HCl	1.293	-2.6	3.47	6.98
69.7	1.0	0.594 HCl	1.796	+0.6	4.64	5.22
69.7	1.0	None	1.659	+9.5	3.93	6.17
52.3	1.0	0.594 HCl	1.791	+1.3	4.60	5.27
52.3	1.0	None	1.671	+8.4	4.00	6.06
5 per cent gelatin	1.0	None	1.153		(3.00)	

arbitrary value, the error thus introduced into the final results is small on account of the fact that the value of $\frac{2UE}{X_a^2/t}$ is small compared to 1.

In deriving equation 1, it was assumed that the mobility of the diffusing ion is constant throughout the system. This is probably a satisfactory approximation in the case of the silica gels, where the ionic strengths of the diffusing solution and of the gel are uniformly high. It probably is not satisfactory for diffusion into gelatin gels or into pure water, where U is some function of X_a and t . In these systems, a calculation of D (taking $E = 0$) should give a value of the "mean" diffusion coefficient of the two ions of the diffusing electrolyte in the medium used. The results in the 5 per cent gelatin gel have been calculated in this way.

The last column of table 1 gives the values of the apparent radius of the

cupric ion as calculated by means of the Stokes-Einstein equation;

$$r = \frac{RT}{N} \frac{1}{6\pi\eta D} \quad (2)$$

In these calculations, η was taken as the viscosity of water (0.00895). While the usefulness of this equation for calculating the radius of an ion has not been established, it has been shown (3) recently that the similar Einstein-Sutherland equation may be used for the calculation of molecular diameters under certain conditions. An excellent discussion of the validity of equation 2 has been given by Williams and Cady (5).

DISCUSSION

In systems which contain cupric chloride in the presence of other soluble chlorides, an appreciable fraction of the cupric ions may be present in the form of complex ions. Thus an error may have been introduced into the calculated values, owing to the fact that the concentration of the cupric ions was assumed to be equal to that of the cupric chloride. However, since the chloride-ion concentration was uniformly high throughout the system, it is probable that the extent of such complex ion formation was relatively constant, and that the value of the concentration ratio which was used in the calculations was practically unchanged. Furthermore, an error of even 10 per cent in the ratio, m_0/m' , would cause an error of only 1 per cent in the value of the diffusion coefficient.

A comparison of the results in the second, third, and fifth lines of table 1, where hydrochloric acid was added to the diffusing solutions in approximately the amounts present in the gels, shows that the highest gel concentration had an appreciable retarding effect on the diffusion process. However, the small difference between the diffusion coefficients in the two more dilute gels indicates that the retarding effect was relatively slight for these gel concentrations, and that the values are practically those which would be obtained in the absence of the gel structure.

The pronounced increase in the diffusion coefficient for a given gel concentration caused by the addition of hydrochloric acid to the diffusing solution seems to illustrate the phenomenon of "accelerated" diffusion discussed by McBain and his coworkers (4). This acceleration was caused by other diffusion processes taking place in the systems. In these silicic acid systems, the diffusion of water was probably negligible. The concentration of the chloride ion was high and relatively uniform throughout the system, and the effect of any spontaneous diffusion of this ion seems to be taken into account in the calculations. However, when no hydrochloric acid was added to the diffusing solution, there was a rapid diffusion of hydrogen and sodium ions from the gel into the solution. Thus the cupric ions diffusing into the gel were retarded by "collision with the molecules

of a diffusing column" (4) of positive ions diffusing spontaneously in the opposite direction. Addition of a suitable amount of hydrochloric acid to the diffusing solution practically eliminated this counter diffusion of hydrogen ions, and enabled the cupric ions to diffuse more nearly at their normal rate. The slight difference caused by the addition of sodium chloride to the diffusing solution at the highest gel concentration indicates that similar compensation for the more slowly diffusing sodium ion is relatively unimportant.

It seems probable, therefore, that the values of the diffusion coefficient obtained in the more dilute gels with hydrochloric acid added to the diffusing solution are very nearly equal to the value for undisturbed diffusion of the cupric ion in water. Likewise, the corresponding values of r probably are accurate approximations of the effective radius of the hydrated cupric ion in so far as the use of the Stokes-Einstein equation is justified for this calculation.

SUMMARY

1. A photometric method has been used to study the diffusion of cupric chloride into gels.
2. The most probable value of the diffusion coefficient of the cupric ion in water is 4.6×10^{-6} cm.² per second.
3. A value of approximately 5.2×10^{-8} cm. is suggested for the effective radius of the hydrated cupric ion in solution.

REFERENCES

- (1) EVERSOLE, W. G., AND DOUGHTY, E. W.: J. Phys. Chem. **39**, 289 (1935).
- (2) EVERSOLE, W. G., AND DOUGHTY, E. W.: J. Am. Chem. Soc. **56**, 1263 (1934).
- (3) HERZOG, R. O., ILLIG, R., AND KUDAR, H.: Z. physik. Chem. **167A**, 329 (1934).
- (4) MCBAIN, J. W., AND DAWSON, C. R.: J. Am. Chem. Soc. **56**, 52 (1934).
MCBAIN, J. W., AND LIU, T. H.: J. Am. Chem. Soc. **53**, 59 (1931).
- (5) WILLIAMS, J. W., AND CADY, L. C.: Chem. Rev. **14**, 171 (1934).

THE SOLUBILITIES AND FREE ENERGIES OF SOME METALLIC SULFIDES

S. FREDERICK RAVITZ

Utah Engineering Experiment Station, University of Utah, Salt Lake City, Utah

Received November 24, 1934

In a recent paper, Kolthoff (18) made a critical survey of the literature regarding the solubilities of metallic sulfides, and pointed out the surprising disparity to be found in the various values reported. He showed that the determinations for each sulfide fall more or less distinctly into two groups, in one of which, represented principally by the results of Weigel (33) and of Biltz (3), the solubilities are of the order of 10^{-6} moles per liter, while in the other, represented principally by the results of Bruner and Zawadzki (6), they are very much less. Kolthoff showed that the values in the first group cannot possibly be correct, and suggested that they might really represent the solubilities of oxidation products present at the surfaces of sulfides. This idea is supported by the well-known fact that oxidation products are usually present at the surfaces of sulfide minerals (27), and by the data in table 1, in which the solubilities of some possible oxidation products of a few of the sulfides (4, 7, 8, 19, 28) are compared with the solubilities of the corresponding sulfides as reported by Weigel.

Kolthoff gave an improved list of solubilities and solubility products, but made no attempt to correct for activities, which, in many cases, cause appreciable changes in the values. Since accurate solubility and free energy data of the more important sulfides are required for research work in pyrometallurgy and in flotation, it was considered advisable to make a careful study of the results of previous investigators, and to recalculate their results with the aid of recent activity data.¹

In order to determine ion-activity coefficients, it has been assumed that the activity coefficients of potassium and chloride ions are equal in potassium chloride solutions, and that the activity coefficient of any ion depends only on the ionic strength (20).

ZINC SULFIDE

Maier (21), using entropy data and the value 43,000 calories (2) for the heat of formation, obtained $\Delta F_{298}^{\circ} = -41,600$ for zinc sulfide. From this,

¹ Unless otherwise specified, free energies, activity data, electrode potentials, and ionization constants are from Lewis and Randall (20).

the solubility product of zinc sulfide is calculated to be 6.4×10^{-23} . These results are rather uncertain, however, owing to considerable uncertainty concerning the heat of formation.

Glixelli (9) has measured the solubility of zinc sulfide in sulfuric acid solutions of various concentrations at 25°C. He found that the zinc sulfide precipitated from alkaline solution (β -ZnS) is several times as soluble as that precipitated from acid solution (α -ZnS); the β -ZnS, however, slowly changes into the α -ZnS, which Glixelli found to be stable, so evidently only the latter should be considered in calculating the solubility product.

TABLE 1

Comparison of solubilities of possible oxidation products of sulfides with Weigel's data for the solubilities of the sulfides

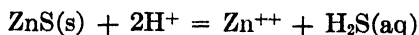
POSSIBLE OXIDATION PRODUCT	SOLUBILITY	SULFIDES	SOLUBILITY (WEIGEL'S DATA)
	<i>moles per liter</i>		<i>moles per liter</i>
Hydrated zinc oxide .	1×10^{-6}	ZnS (ppt.) ..	0.71×10^{-6}
Zinc oxide .	36×10^{-6}	Sphalerite.	6.6×10^{-6}
Lead carbonate	4.0×10^{-6}	PbS (ppt.) ..	3.6×10^{-6}
Lead oxide... ..	6.3×10^{-6}	Galena .	1.2×10^{-6}
Copper carbonate	55×10^{-6}	CuS	3.5×10^{-6}
(CuO·0.515CO ₂ ·0.61H ₂ O).	13×10^{-6}	Cu ₂ S.....	3.1×10^{-6}

TABLE 2

Equilibrium constants for solubility of zinc sulfide in sulfuric acid

H ₂ SO ₄ CONCENTRATION	(H ₂ S) × 10 ⁴	μ	(H ⁺)	α _{Zn}	K ₁ × 10 ⁴
<i>formal</i>	<i>moles per liter</i>				
0.001	0.024	0.00275	0.00178	0.72	1.31
0.01	0.207	0.0205	0.01393	0.52	1.15
0.05	0.927	0.0844	0.05672	0.36	0.96
0.25	4.376	0.35	0.25	0.24	0.74
Mean.....					1.04

For the solubility equilibrium



the equilibrium constant is

$$K_1 = (\text{Zn}^{++}) (\text{H}_2\text{S}) / (\text{H}^+)^2$$

In table 2 are shown the results of the recalculations of Glixelli's data. The ionic strengths (μ) and the hydrogen-ion activities (H⁺) were calcu-

lated from the data of Sherrill and Noyes (30) for acid concentrations of 0.05 molal and less; the activity of hydrogen ion in 0.25 molal sulfuric acid was estimated to be 0.25. The activity coefficients of zinc ion (α_{Zn}) were calculated from the data of Lewis and Randall on potassium chloride and of Scatchard and Tefft (29) on zinc chloride.

In a similar way, the value of $K_1 = 0.91 \times 10^{-4}$ was calculated from the results of Moser and Behr (24), who found the solubility of zinc sulfide (precipitated by hydrogen sulfide from zinc sulfate solution) to be 6.34×10^{-3} moles per liter in 1 molal sulfuric acid saturated with hydrogen sulfide at atmospheric pressure and 20°C. It has been assumed that the decrease in solubility of hydrogen sulfide from 20°C. to 25°C. was approximately compensated by the increase in solubility of the zinc sulfide.

Although the sulfuric acid concentration varies 1000-fold in the two sets of data, the extreme variation of the equilibrium constant is only 1.8-fold. The value $K_1 = 1.0 \times 10^{-4}$ is therefore probably quite reliable. From this value it is found that the solubility product of zinc sulfide is 1.5×10^{-26} and $\Delta F_{298}^\circ = -46,960$; with the aid of Maier's entropy data, the value of ΔH is found to be $-48,355$.

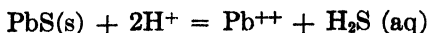
LEAD SULFIDE

Unfortunately, there are few data available from which an accurate value for the solubility product of lead sulfide can be calculated. Bruner and Zawadzki (6) measured the solubility of lead sulfide in hydrochloric acid solutions and obtained $K_1 = 3.1 \times 10^{-6}$, which corresponds to a solubility product of 3.6×10^{-28} . They give no experimental data, however, but merely state that their result was obtained from several experiments which agreed well with each other; it is impossible, therefore, to recalculate their value.

Jellinek and Czerwinski (14), from measurements of the potentials of a lead electrode in sodium sulfide solutions, obtained values from 6.4×10^{-15} to 13.0×10^{-15} for the solubility product of lead sulfide, and from similar measurements in sodium hydrosulfide solutions, obtained values from 1.4×10^{-13} to 5.0×10^{-13} . Trumpler (31), however, has shown that lead electrodes in sulfide solutions do not exhibit their true potentials, and by making the proper corrections he obtained the value 15×10^{-30} from measurements of the potential of a lead electrode in 2 *N* sodium sulfide solution.

Trumpler also found that the highest concentration of hydrochloric acid saturated with lead chloride from which lead sulfide can be precipitated by hydrogen sulfide at atmospheric pressure is 2 normal; from this he calculated the solubility product to be 4.9×10^{-29} . A much more accurate value can be calculated with the aid of activity data. From the

data of Lewis and Randall on the solubility of lead chloride and on the activity coefficients of hydrochloric acid, and of Harned on the activity coefficients of potassium chloride (10), the value $K_1 = 7.87 \times 10^{-8}$ is obtained for the equilibrium



which corresponds to the value 9.05×10^{-30} for the solubility product of lead sulfide.

Maier (23) has recently calculated from the thermal data of Jellinek and Zakowski (16) and of Jellinek and Deubel (15) the value $\Delta F_{298}^\circ = -21,977$ for the free energy of formation of lead sulfide. From this the solubility product of lead sulfide is found to be 7.00×10^{-30} , which agrees excellently with the value calculated above.

COPPER SULFIDES

Except for the values of Weigel and of Biltz, the only determinations of the solubility of cupric sulfide seem to have been made by measuring the potentials of copper electrodes in sulfide solutions against a normal calomel electrode. From such electromotive force measurements by Immerwahr (11) and by Knox (17), Bruner and Zawadzki (6) calculated the values 5.9×10^{-42} and 1.2×10^{-42} , respectively; Jellinek and Czerwinski (14) from similar measurements obtained values from 1.0×10^{-42} to 5.0×10^{-42} . In spite of the agreement among these results, they very probably are incorrect, since Trumpler (31) has shown that in strong sulfide solutions the only stable copper sulfide is Cu_2S .

Cupric sulfide

Randall, Nielson, and West (26) have calculated the free energy of formation of cupric sulfide to be $-11,755$. This corresponds to 3.48×10^{-38} for the solubility product. If the other values given above for the solubility product were correct, the free energy value of Randall, Nielson, and West would be in error by more than 5000 calories, whereas it very probably is correct to within less than 1000 calories.

Cuprous sulfide

It was pointed out above that the measurements of Jellinek and Czerwinski are inapplicable to cupric sulfide. Their measurements can be used, however, to calculate the solubility product of cuprous sulfide, and seem to be the best available for this purpose. They give quite complete data, but unfortunately their experiments were performed at 10°C . Since there are no data from which the electrode potential of cuprous ion at 10°C . can be obtained, it appears that the best procedure is to use the 25°C .

values for the electrode potentials of cuprous ion² and of the normal calomel electrode (against which Jellinek and Czerwinski made their measurements). This is equivalent to assuming that the potentials of these two electrodes change approximately the same amount in passing from 25°C. to 10°C., which is not improbable.

The sulfide-ion concentrations in sodium sulfide and in sodium hydrosulfide solutions as given by Jellinek and Czerwinski are undoubtedly incorrect. Much more accurate values can be determined from the ionization constants of hydrogen sulfide and of water at 10°C., which can readily be calculated from the data of Lewis and Randall.

In evaluating the sulfide-ion concentrations, the ionic strength of sodium sulfide has been taken as twice its molality (since it is almost completely

TABLE 3
Solubility product of cuprous sulfide at 10°C.

MOLAL CONCENTRATION	E_c IN VOLTS	$(\text{Cu}^+) \times 10^{24}$	$(\text{S}^{--}) \times 10^5$	$K_{\text{Cu}_2\text{S}} \times 10^{21}$
(a) Na_2S				
0.5	1.131	0.395	656.0	1.02
0.1	1.100	1.41	56.2	1.13
0.05	1.079	3.33	15.6	1.73
0.01	1.060	7.25	0.792	0.417
0.005	1.041	15.8	0.212	0.529
Mean				0.963
(b) NaHS				
0.5	0.990	128.0	0.436	71.3
0.1	0.982	177.0	0.0559	17.5
0.05	0.980	193.0	0.0212	7.91

hydrolyzed to sodium hydroxide and sodium hydrosulfide), and that of sodium hydrosulfide as equal to its molality; the activity coefficients of hydrosulfide ion and of hydroxyl ion have been assumed to be equal, and have been calculated from data given by Lewis and Randall for potassium hydroxide.

In table 3 are shown the results of the calculations. The column headed E_c gives the potentials against the normal calomel electrode as determined by Jellinek and Czerwinski. The constants obtained from the measurements in sodium hydrosulfide solutions are rather inconsistent, and differ considerably from those obtained from the measurements in sodium sulfide solutions. Jellinek and Czerwinski prepared their sodium

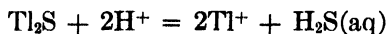
² $E^\circ = -0.522$. Fenwick: J. Am. Chem. Soc. **48**, 860 (1926).

hydrosulfide solutions by saturating a sodium hydroxide solution of definite concentration with hydrogen sulfide, sweeping out the excess hydrogen sulfide with a stream of hydrogen, and diluting to the desired concentration. It is possible, however, that the removal of hydrogen sulfide was incomplete, for it is very interesting to note that if it is assumed that an excess of 1 per cent of hydrogen sulfide is present, the following values for the solubility product of cuprous sulfide are obtained from the three sodium hydrosulfide solutions, respectively: 1.88×10^{-51} , 1.21×10^{-51} , and 0.774×10^{-51} . These figures agree well not only with each other, but also with those obtained from the sodium sulfide solutions.

Randall, Nielson, and West (26) have calculated the free energy of formation of cuprous sulfide as $-19,955$ at $25^\circ\text{C}.$, which corresponds to 36×10^{-51} for the solubility product. The agreement between this value and the value 1.0×10^{-51} obtained above for $10^\circ\text{C}.$ may be considered quite satisfactory, since an increase of 3.3-fold in the solubility of cuprous sulfide in passing from $10^\circ\text{C}.$ to $25^\circ\text{C}.$ would account for the difference.

THALLOUS SULFIDE

The solubility product of thallous sulfide can be recalculated from the complete data given by Bruner and Zawadzki (6) for the equilibrium



They obtained $K_1 = 0.637$. They reached equilibrium by four methods: by precipitating the sulfide with hydrogen sulfide at a pressure of one atmosphere from neutral or slightly acidified solutions of (a) thallous sulfate and (b) thallous nitrate; (c) by dissolving thallous sulfide in sulfuric acid solutions in the presence of hydrogen sulfide at atmospheric pressure; and (d) by dissolving thallous sulfide in sulfuric acid in sealed tubes, in which case thallous ion and hydrogen sulfide are present in equivalent amounts.

In making the calculations, only solutions in which the ionic strength was less than 0.1 have been considered. The hydrogen-ion activities were determined from the data of Sherrill and Noyes (30) for sulfuric acid solutions; activity coefficients for thallous ion were obtained from Lewis and Randall.

In their experiments with sealed tubes (method d), Bruner and Zawadzki measured both the thallous-ion and hydrogen sulfide concentrations at equilibrium, and used both in their calculations. The values for the two should be exactly equivalent, but the values they obtained for hydrogen sulfide are consistently low. The recalculations are based on the thallium determinations, which are probably the more reliable.

The results of the calculations are summarized in table 4. The solutions considered cover a sixfold range of thallous-ion concentrations, and a

sevenfold range of hydrogen-ion concentrations. The values of K_1 all agree quite well, although those obtained from method b are somewhat high. If the latter are discarded, the composite mean becomes 0.520 with an average deviation of 5.70 per cent and a maximum deviation of 11.92 per cent; there seems to be no valid reason to discard them, however. The mean, 0.556, corresponds to 6.39×10^{-23} for the solubility product and $-22,365$ for the free energy of formation of thallous sulfide.

Moser and Behr (24) have obtained 0.00329 mole per liter as the mean of several measurements of the solubility of thallous sulfide in 0.005 *M* sulfuric acid saturated with hydrogen sulfide at atmospheric pressure and 20°C. Assuming, as in the case of zinc sulfide, that the decrease in solubility of hydrogen sulfide at 25°C. is balanced by an increase in the solubility of thallous sulfide, the value of K_1 is calculated to be 0.42, which agrees reasonably well with the more reliable value found above.

TABLE 4

Equilibrium constants for solubility of thallous sulfide in acid solutions

EQUILIBRIUM METHOD	NUMBER OF EXPERIMENTS	MEAN VALUE OF K_1	AVERAGE DEVIATION FROM MEAN	MAXIMUM DEVIATION FROM MEAN
			<i>per cent</i>	<i>per cent</i>
a	10	0.510	4.82	9.22
b	4	0.712	5.13	7.30
c	3	0.560	4.11	6.07
d	4	0.510	6.42	10.20
Composite	21	0.5556	11.53	37.51

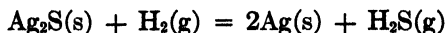
SILVER SULFIDE

From data given by Jellinek and Czerwinski (14) on the potentials of a silver electrode in sodium sulfide solutions at 10°C., the solubility product of silver sulfide can be calculated in the same manner as for cuprous sulfide. In this case, however, information is available from which the electrode potential of silver at 10°C. can be determined. For silver ion, $\Delta H_{298} = 24,870$ (12). Assuming this to be constant between 25°C. and 10°C., the electrode potential of silver at 10°C. is calculated to be -0.8206 volt. For the half-cell $\text{Hg}, \text{HgCl}, \text{Cl}^-$, $\Delta H_{298} = 8291$ (Lewis and Randall (20)), and from this, the potential of the normal calomel electrode at 10°C. is calculated to be -0.2862 volt. Using these values, the silver-ion concentrations in table 5 were obtained; the sulfide-ion concentrations were determined in the consideration of cuprous sulfide.

From the mean value, 1.04×10^{-54} , of the solubility product at 10°C., its value at 25°C. can be calculated with the aid of the values of ΔH for silver sulfide, silver ion, and sulfide ion. These are -5022 , $24,870$, and $10,043$, respectively (13). Assuming these to be constant between 10°C.

and 25°C., the solubility product is calculated to be 3.28×10^{-52} , which corresponds to -9930 for the free energy of formation of silver sulfides.

The equilibrium



has been investigated at temperatures from about 450°C. to 700°C. by Watanabe (32), who found $\Delta F_{298}^\circ = -9098$ for the formation of silver sulfide. This determination, however, probably involved a long extrapolation with the aid of somewhat uncertain heat capacity data. Noyes and Freed (25) have made a careful study of the same equilibrium at 25°C. and obtained values from -1350 to -2116 for the standard free energy change of the reaction. The free energy of formation of hydrogen sulfide is -7840 , hence the corresponding values of the free energy of formation

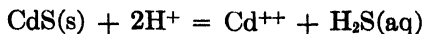
TABLE 5
Solubility product of silver sulfide at 10°C.

CONCENTRATION OF Na_2S	E_e	$(\text{Ag}^+) \times 10^{28}$	$(\text{S}^{--}) \times 10^4$	$K_{\text{Ag}_2\text{S}} \times 10^{54}$
<i>molar</i>	<i>volts</i>			
0.5	0.928	0.922	656.0	0.558
0.1	0.8895	4.47	56.2	1.12
0.05	0.869	10.35	15.6	1.67
0.01	0.842	31.3	0.792	0.776
0.005	0.822	71.1	0.212	1.07
Mean.....	1.04

of silver sulfide are from -9190 to -9956 . The value -9930 , calculated from the solubility product, thus falls between these two values.

CADMIUM SULFIDE

There seem to be no very reliable data from which the free energy or solubility product of cadmium sulfide can be accurately determined. Bruner and Zawadzki (6) studied the equilibrium



under several different conditions and obtained $K_1 = 4.6 \times 10^{-7}$ for cadmium sulfide formed from cadmium sulfate, and $K_1 = 6.6 \times 10^{-6}$ for cadmium sulfide formed from the chloride; these values correspond to solubility products of 5.3×10^{-29} and 7.6×10^{-28} , and free energies of formation of $-34,106$ and $-31,915$, respectively. They state that their constants varied rather widely, and that the solid phase did not appear to be well-defined, varying from red to yellow according to the precipitation

conditions and the duration of the experiments. Since they give no experimental data, their results cannot be recalculated.

Aumeras (1) recently obtained the value $K_1 = 1.06 \times 10^{-6}$ for the above equilibrium by measuring the solubility of cadmium sulfide (precipitated from the chloride) in hydrochloric acid solutions (0.24 *N* to 0.885 *N*) in the presence of varying concentrations of hydrogen sulfide; the cadmium concentration varied from 0.00025 *M* to 0.003 *M*. These measurements, however, seem to be quite unsuitable for the determination of K_1 , since Lewis and Randall (20) have shown that the activity coefficient of cadmium chloride becomes decidedly abnormal at concentrations greater than about 0.0005 *M*, and this effect would undoubtedly be greatly enhanced in the presence of relatively strong hydrochloric acid.

Maier (22), from entropy data and Thomsen's value, $\Delta H = -34,350$, for cadmium sulfide has calculated the free energy of formation to be $-33,038$.

TABLE 6
Free energy and solubility data for sulfides

SULFIDE	TEMPERATURE	ΔF°	SOLUBILITY PRODUCT	SOLUBILITY IN WATER
	$^\circ\text{C}$			<i>moles per liter</i>
ZnS	25	-46,960	1.15×10^{-26}	1.47×10^{-9}
PbS	25	-21,977	7.00×10^{-30}	3.62×10^{-11}
CuS	25	-11,755	3.48×10^{-38}	2.55×10^{-15}
Cu ₂ S	25	-19,995	3.60×10^{-50}	1.19×10^{-14}
Tl ₂ S	25	-22,365	6.39×10^{-23}	3.55×10^{-6}
Ag ₂ S	25	-9,930	3.28×10^{-52}	2.48×10^{-15}
CdS	25	-33,038	1.14×10^{-28}	1.46×10^{-10}
Cu ₂ S	10		1.0×10^{-51}	4.24×10^{-15}
Ag ₂ S	10		1.04×10^{-54}	4.29×10^{-15}

Britzke and Kapustinsky (5), from equilibrium measurements of the reduction of cadmium sulfide by hydrogen at high temperatures, obtained $\Delta H_{298} = -19,800$, and they suggest the possibility that cadmium sulfide precipitated from solution may have the composition Cd(CdS₂) at room temperature, dissociating into CdS at higher temperatures. In view of the agreement between Maier's free energy value and those calculated from the results of Bruner and Zawadzki, it appears that the former ($-33,038$) is the most reliable value available at the present time for precipitated cadmium sulfide.

RÉSUMÉ

In table 6 are listed the values recommended for the standard free energies of formation, the solubility products, and the solubilities in water of the sulfides which have been considered.

REFERENCES

- (1) AUMERAS: J. chim. phys. **25**, 727 (1928).
- (2) BERTHELOT: Ann. chim. phys. [5] **4**, 187 (1875).
- (3) BILTZ: Z. physik. Chem. **58**, 288 (1907).
- (4) BOTTGER: Z. physik. Chem. **46**, 521 (1903).
- (5) BRITZKE AND KAPUSTINSKY: Z. anorg. Chem. **194**, 349 (1930).
- (6) BRUNER AND ZAWADZKI: Z. anorg. Chem. **65**, 136 (1909).
- (7) DUPRE AND BIALAS: Z. angew. Chem. **16**, 55 (1903).
- (8) FREE: J. Am. Chem. Soc. **30**, 1366 (1908).
- (9) GLIXELLI: Z. anorg. Chem. **55**, 297 (1907).
- (10) HARNED: J. Am. Chem. Soc. **51**, 416 (1929).
- (11) IMMERWAHR: Z. Elektrochem. **7**, 478 (1901).
- (12) International Critical Tables, Vol. V, p. 188. McGraw-Hill Book Co., New York (1929).
- (13) Reference 12, pp. 177 and 188.
- (14) JELLINEK AND CZERWINSKI: Z. physik. Chem. **102**, 438 (1922).
- (15) JELLINEK AND DEUBEL: Z. Elektrochem. **35**, 451 (1929).
- (16) JELLINEK AND ZAKOWSKI: Z. anorg. Chem. **142**, 1 (1925).
- (17) KNOX: Trans. Faraday Soc. **4**, 30 (1908).
- (18) KOLTHOFF: J. Phys. Chem. **35**, 2711 (1931).
- (19) KOLTHOFF AND KAMEDA: J. Am. Chem. Soc. **53**, 832 (1931).
- (20) LEWIS AND RANDALL: Thermodynamics, pp. 380-1. McGraw-Hill Book Co., New York (1923).
- (21) MAIER: U. S. Bureau of Mines, Bulletin 324, p. 27 (1930).
- (22) MAIER: U. S. Bureau of Mines, R. I. 3218, p. 32 (1933).
- (23) MAIER, C. G.: Unpublished report entitled "The Contamination of Gold Surfaces by Lead Compounds in Roasting Galena-containing Auriferous Pyrite." Private communication to the author.
- (24) MOSER AND BEHR: Z. anorg. Chem. **134**, 49 (1924).
- (25) NOYES AND FREED: J. Am. Chem. Soc. **42**, 476 (1920).
- (26) RANDALL, NIELSON, AND WEST: Ind. Eng. Chem. **23**, 388 (1931).
- (27) See, for example, RAVITZ AND PORTER: Am. Inst. Mining Met. Engrs. Tech. Pub. 513, p. 4 (1933).
- (28) REMY AND KUHLMANN: Z. anal. Chem. **65**, 161 (1924).
- (29) SCATCHARD AND TEFFT: J. Am. Chem. Soc. **52**, 2272 (1930).
- (30) SHERRILL AND NOYES: J. Am. Chem. Soc. **48**, 1870 (1926).
- (31) TRUMPLER: Z. physik. Chem. **99**, 9 (1921).
- (32) WATANABE: Bull. Inst. Phys. Chem. Research Tokyo **8**, 708 (1929); cf. Chem. Abstracts **24**, 289 (1930).
- (33) WEIGEL: Z. physik. Chem. **58**, 283 (1907).

VISCOSITY RELATIONSHIPS IN EMULSIONS CONTAINING MILK FAT

ABRAHAM LEVITON AND ALAN LEIGHTON

Research Laboratories, Bureau of Dairy Industry, U. S. Department of Agriculture, Washington, D. C.

Received March 8, 1935

On the basis of theoretical hydrodynamics, the viscosity of a dilute emulsion is a linear function of the volume percentage of the dispersed phase, and is independent of particle size. The equation derived by Taylor (4) expressing this relationship is:

$$\frac{\eta}{\eta_0} = 1 + 2.5 \frac{\eta' + \frac{2}{5} \eta_0}{\eta' + \eta_0} V$$

where η = viscosity of emulsion,

η_0 = viscosity of continuous medium,

η' = viscosity of dispersed phase, and

V = ratio of volume of dispersed phase to total volume.

When η' is infinite, i.e., when the suspended phase is solid, the equation becomes identical with the Einstein formula governing the viscosity relationships in a suspension of solid spheres.

The applicability of equation 1, as well as the Einstein equation, is limited by the assumptions underlying the theoretical development of these equations.

Smoluchowski (3) has pointed out that the range of concentration over which the Einstein equation is applicable is so narrow that the accuracy with which viscosity may be measured is insufficient to establish the validity of the equation, and that consequently an investigation of a suspension over a wide range of concentration, leading to the development of an empirical relationship, is desirable. Such a relationship, according to Smoluchowski, should be reducible for very small concentrations to the relationship expressed in the Einstein equation, and should be generally applicable to suspensions of spherical particles.

For various reasons, and under certain experimental conditions which will be discussed in other parts of this paper, viscosity data obtained in the investigation of milk and related emulsions should be susceptible to treatment on the basis of the conclusions drawn from investigations in theoretical hydrodynamics, provided that in the emulsions under investiga-

tion the medium containing the ingredients other than fat may properly be regarded as the continuous medium. An empirical equation developed for these emulsions should be generally applicable to suspensions of spherical particles.

In view of the foregoing considerations, an investigation was undertaken of the viscosity of emulsions containing milk fat suspended in skim milk, in diluted skim milk, in concentrated skim milk, and in a very viscous solution of sucrose in skim milk; first, in order to establish empirically the relationship existing between the following: (1) the viscosity of an emulsion and the concentration of the dispersed phase, (2) the viscosity of an emulsion and the composition of the continuous medium, and (3) the viscosity of an emulsion and the degree of dispersion of the dispersed phase; and, finally, in order to discuss the significance of these empirical relationships.

EXPERIMENTAL

Smoluchowski (3) has pointed out that, in order to test the validity of the Einstein equation, it is necessary to work with suspensions in which the hydrodynamical volume of the suspended material does not differ measurably from the actual volume because of the association of part of the continuous medium with the suspended material. Inasmuch as the clumping of the fat globules is a phenomenon usually encountered in milk and related emulsions, which would contribute towards an increase in the apparent volume of the suspended material, it is necessary to work under conditions such that the clumping is minimized to the extent where its effect on viscosity is entirely negligible. For this reason viscosity measurements by means of a capillary pipet were made at 64°C. on samples stirred uniformly and continuously prior to measurement. The stirring, carried out in such a manner as to avoid the incorporation of air, permitted of uniformity in the distribution of the fat phase, and minimized the probability of the formation of stable clumps.

The temperature of the measurement was selected as one at which, according to the results of Troy and Sharp (5), fat clusters do not form at all in unhomogenized milk, and at which those that are present tend to disintegrate. It may be observed, by means of a microscope, that when milk at approximately this temperature flows through a capillary under the application of a very slight pressure head, the fat globules, as they move past the field under observation, are dispersed as single globules. Although rigid proof of the complete absence of clumps in the more concentrated emulsions is extremely difficult, if not impossible, to obtain, yet, if the empirical equation developed from the viscosity data obtained in the investigation of these emulsions is reducible to the Taylor equation,

then it may safely be inferred that the extent of clumping, if clumps are present at all, is small enough to be entirely negligible.

A part of the mix under investigation was forced up under a known pressure into the viscosimeter, the capillary tubing of which was for the most part immersed in the sample, although partly surrounded by a hot-air jacket. Precautions were taken that the temperature of the capillary should be the same as that of the mix prior to the application of pressure.

The pressure at which the determination was made was corrected to compensate for the back head created as the fluid rose in the pipet. The corrected mean pressure was obtained by means of the following formula:

$$P_m = \frac{(h_2 - h_1)d}{2.303 \log \frac{P_0 - h_1d}{P_0 - h_2d}}$$

where P_m = the mean pressure,

d = the density,

P_0 = the recorded pressure,

h_1 = the distance between the top of the capillary and the top mark of the pipet, and

h_2 = the distance between the level of the fluid in the container and the top mark of the pipet.

The formula may be easily derived and shown to be applicable to the viscosity data reported in this paper.

Viscosity values were calculated by means of the following fundamental equation for flow through a capillary tube as determined by Poiseuille, and amplified by Couette:

$$\eta = K_1Pt - \frac{K_2}{t}$$

where η = the viscosity,

P = the pressure difference causing flow,

t = the time required for a definite volume of fluid to enter the viscosimeter, and

K_1 and K_2 = constants, the values of which depend on the dimensions of the viscosimeter.

In one experiment the pressure was halved in order to note whether the mixes were truly viscous. No indication was found of the existence of any significant plastic effects.

The pressures used in the various measurements ranged from 78.1 to 183.9 g. per square centimeter, depending on the viscosity of the mixes investigated. Both too rapid, as well as too slow, rates of flow were

avoided, since these were conditions conducive to turbulent flow on one hand and to creaming on the other.

Composition of emulsions

In order to ascertain the relationship existing between the viscosity of an emulsion and its fat percentage when the composition of the continuous medium is varied, the following series of emulsions were investigated:

- I. (a) Cream containing 36.5 per cent fat; (b) skim milk containing 0.02 per cent fat; (c) emulsions containing (a) and (b) in the following proportions: 3:1, 2:1, 1:3, 1:5.
- II. (a) Emulsion containing 20 per cent fat, 30 per cent skim milk, and 50 per cent water; (b) suspension containing 50 parts water to 30 parts skim milk; (c) emulsions containing (a) and (b) in the following proportions: 4:1, 3:2, 2:3, 1:4.
- III. (a) Emulsion containing 20 per cent fat, 30 per cent skim milk, and 50 per cent condensed skim of a 28.6 per cent milk-solids-not-fat content; (b) suspension containing 50 parts condensed skim milk of a 28.6 per cent solids content to 30 parts skim milk; (c) emulsions containing (a) and (b) in the following proportions: 4:1, 3:2, 2:3, 1:4.
- IV. (a) Emulsion containing 28 per cent fat, 42 per cent skim milk, 30 per cent cane sugar; (b) suspension containing 30 parts cane sugar to 42 parts skim milk; (c) emulsions containing (a) and (b) in the following proportions: 4:1, 3:2, 2:3, 1:4.

All emulsions in each of the series were derived from skim milk and cream obtained from the same batch of fresh whole milk. Fat determinations (Babcock) in triplicate on samples taken from the cream used in the preparation of the various mixes served as a basis for the calculation of the fat percentage of the various mixes. The densities of the various suspensions containing no fat, that is, of the continuous media, were determined at 64°C. From these values and that of the density of milk fat at 64°C., as recorded in the literature, the densities of the various emulsions were calculated.

In each of the series of emulsions I, II, III, and IV, only the fat percentage was varied. In the emulsions of series I, II, and III, the continuous medium consisted of skim milk, diluted skim milk, and concentrated skim milk, respectively. In the emulsions of series IV, the continuous medium contained, in addition to the skim milk, sufficient cane sugar to give a rather viscous suspension. The variations in the composition of the continuous medium were such that a very wide range of viscosity values belonging to the continuous medium was obtained. These variations were necessary to the development of an empirical relationship of wide applicability and of theoretical significance. The results of viscosity measurements on the various emulsions are given in table 1.

TABLE 1
Relationship between viscosity and fat content of various emulsions

EMULSION SERIES NO. (SEE P. 74)	FAT CON- CENTRA- TION	DENSITY* OF MILK FAT AT 64°C.	DENSITY OF EMULSION	VOLUME OF FAT PER CC. OF EMULSION	η' , APPROXI- MATE VISCOSITY OF FAT†	P_m , MEAN PRESSURE USED IN VISCOSITY MEASUREMENT	η , VISCOSITY OF EMULSIONS	$\frac{2.5 \left(\eta' + \frac{2}{5} \eta_0 \right)}{\eta' + \eta_0}$	$\frac{\eta}{\eta_0}$ (MEASURED)	$\frac{\eta}{\eta_0}$ CALCULATED BY MEANS OF EQUATION 2
I	per cent			cc.	centipoises	grams per cm ³	centipoises			
	36.5	0.8887	0.9652	0.397	14.0	147.5	3.117	2.44	4.84	4.82
	27.4	0.8887	0.9766	0.302	14.0		1.952		3.03	3.00
	18.3	0.8887	0.9889	0.204	14.0		1.281		1.99	1.97
	9.1	0.8887	1.002	0.103	14.0		0.872		1.35	1.35
II	6.1	0.8887	1.008	0.069	14.0		0.777		1.21	1.21
	0.0	0.8887	1.015	0.000	14.0		0.644 (η_0)			
	20.0	0.8887	0.970	0.218	14.0	78.1	0.986	2.45	2.07	2.09
	16.0	0.8887	0.975	0.177	14.0		0.857		1.80	1.78
	12.0	0.8887	0.979	0.132	14.0		0.697		1.49	1.49
III	8.0	0.8887	0.983	0.0889	14.0		0.612		1.29	1.29
	4.0	0.8887	0.988	0.0447	14.0		0.532		1.12	1.13
	0.0	0.8887	0.993	0.000	14.0		0.476 (η_0)			
	20.0	0.8887	1.021	0.230	14.0	137.5	2.506	2.39	2.21	2.19
	16.0	0.8887	1.029	0.185	14.0		2.047		1.81	1.81
IV	12.0	0.8887	1.037	0.140	14.0		1.739		1.54	1.53
	8.0	0.8887	1.045	0.0941	14.0		1.490		1.31	1.32
	4.0	0.8887	1.053	0.0474	14.0		1.270		1.12	1.14
	0.0	0.8887	1.061	0.000	14.0		1.134 (η_0)			
	28.0	0.8887	1.090	0.343	14.0	182.9	8.427	2.27	3.35	3.34
	22.4	0.8887	1.111	0.280	14.0		6.409		2.55	2.53
	16.8	0.8887	1.130	0.214	14.0		4.800		1.91	1.94
	11.2	0.8887	1.150	0.145	14.0		3.818		1.52	1.52
	5.6	0.8887	1.172	0.0739	14.0		3.064		1.22	1.22
	0.0	0.8887	1.195	0.000	14.0		2.512 (η_0)			

* Value obtained from work of Rahn: *Milchwirtschaft. Forsch.* **3**, 512 (1926).

† Value obtained from work of White and Twining: *J. Ind. Eng. Chem.* **5**, 568 (1913).

In order to ascertain the relationship existing between the viscosity of an emulsion and the degree of dispersion of the fat phase the following emulsions were investigated: (I) cream containing 10 per cent fat and 1 part of sodium citrate per 100 parts of mix; (II) emulsion containing 10 per cent fat, $23\frac{1}{2}$ per cent skim milk, $66\frac{2}{3}$ per cent water, and 100 grams of sodium citrate per 30 pounds of mix.

These emulsions were heated to 60°C. and divided into two portions; one portion was homogenized at 2500 pounds, and rehomogenized at 500 pounds pressure. Viscosity measurements were then made on the homogenized and unhomogenized portions of emulsion I. The mixes obtained from emulsion II were condensed under vacuum to contain approximately 40 per cent fat, after which they were standardized to contain exactly 30 per cent fat. Viscosity measurements were then made on these emulsions.

TABLE 2

Showing effect of an increase in dispersion of fat globules on viscosity

FAT CONCENTRATION	DIAMETER OF FAT GLOBULES	PRESSURE USED IN VISCOSITY MEASUREMENT	TIME OF FLOW			VISCOSITY AT 64°C.
			sec.	sec.	sec.	
<i>per cent</i>	μ	grams per cm. ²				<i>centipoises</i>
30	3	145 0	59 6	59 6	59 4	2.476
30	0 7	145.0	59 8	59 5	59 4	2.476
10	3	152 0	24 6	24 7	24 7	0.924*
10	0 7	152 0	24 6	24.7	24 7	0.924

* Viscosimeters used for 10 per cent mixes and 30 per cent mixes differed.

Microscopic observations under a magnification of 800 to determine the average size of the fat globules were made on samples diluted 1:200 and mounted as hanging drops. These results, together with the results of viscosity measurements, are tabulated in table 2.

The addition of sodium citrate to the emulsions, and subsequent rehomogenization, serve to render decidedly unfavorable the chances for the formation and the existence of clumps. Thus, Hening and Dahlberg (2) report that the addition of sodium citrate to an ice cream mix prior to homogenization serves to reduce the size and the number of clumps in the homogenized mix, while rehomogenization is well known as a means to disintegrate the clusters formed during homogenization.

DISCUSSION

That the suspensions containing no fat may be considered identical in composition with the continuous media of the corresponding emulsions containing fat presupposes that the extent to which protein is adsorbed

by the fat is negligible. Evidence exists to support such an assumption. The ratio of water to milk-solids-not-fat in cream, according to information contained in *Fundamentals of Dairy Science* (1) has repeatedly been demonstrated to be the same as the ratio in the milk from which the cream was produced. Proof of a more decisive character to justify the assumption, however, may be obtained from the investigation of Troy and Sharp (5), who report that the variation of the rate of rise of individual fat globules in milk with variations in the radius of the globules obeys quite exactly Stokes' law. This conformation to Stokes' law should have its counterpart in the conformation to Taylor's equation, in the case of dilute emulsions, of the viscosity data reported in this manuscript.

Table 1, which gives the results of the viscosity measurements on emulsions varying in their fat content and in the composition of the continuous medium, also gives the values calculated from the following relationship deducible from these results:

$$\ln \frac{\eta}{\eta_0} = 2.5 \left(\frac{\eta' + \frac{2}{5} \eta_0}{\eta' + \eta_0} \right) (V + V^{\frac{5}{3}} + V^{\frac{11}{3}}) \quad (2)$$

where the significance of the terms may be obtained by reference to equation 1. It is readily seen that for small values of V the equation may be reduced to:

$$\frac{\eta}{\eta_0} = 1 + 2.5 \frac{\eta' + \frac{2}{5} \eta_0}{\eta' + \eta_0} V$$

which is identical with the equation derived by Taylor on the basis of theoretical hydrodynamics.

In connection with the power series involving V , and occurring in the exponent of equation 2, it may be explained that $V^{\frac{5}{3}}$ is included as the next term in the series in conformity with the suggestion of Smoluchowski (3) that, if the development of the Einstein equation is extended to apply not only to very dilute suspensions but also to more concentrated ones, the series development involving V should include, in addition to V , $V^{\frac{5}{3}}$ as a very close approximation to the next term. The third term, $V^{\frac{11}{3}}$, in the series has no theoretical significance, and is included in order to effect an agreement between the measured and calculated values of η , for the emulsions containing comparatively high concentrations of fat.

The form of the equation and the constant occurring in it are independent of the milk-solids-not-fat content of the continuous medium. The equation may be reduced for dilute emulsions to that derived by Taylor, regardless of the composition or the viscosity of the continuous medium. Consequently, the designation of the suspension, containing particles small in size relative to the fat globules, as the continuous medium

is justified, and the validity of the application of Taylor's equation to the emulsions under investigation may be considered to be established. The multiplication of the constant 2.5 in the Einstein equation by the term

$$\frac{\eta' + \frac{2}{3}\eta_0}{\eta' + \eta_0}$$

to compensate for the currents set up within the particle, when the dispersed phase is fluid, is supported experimentally by the results given in table 1. Thus, η_0 may be varied by the addition of water, condensed skim milk, or cane sugar to skim milk, so that the expression

$$\frac{\eta' + \frac{2}{3}\eta_0}{\eta' + \eta_0}$$

is varied from 2.27 to 2.45, and yet the calculated values of the ratio between the viscosity of the emulsion and that of the continuous medium agree within experimental error with the measured values.

Considered together with the evidence already offered in the experimental part, the fact that empirical equation 2 is reducible to the theoretical equation may be taken as proof that the extent of clumping is insignificant, not only in the dilute emulsions under investigation but also in the more concentrated ones.

The results contained in table 2, concerning the effects of subdivision of the fat globules on the viscosity of the emulsions containing 10 per cent and 30 per cent fat, indicate that, within the limits of experimental error, no measurable increase in viscosity attends a fourfold reduction in the diameter of the fat globules, in agreement with the theoretical demands implicit in equation 1. This independence of viscosity with respect to the size of the fat globules indicates that the viscosity relationships obtained for the unhomogenized emulsions may be applied without change to the corresponding homogenized emulsions, provided of course that the homogenized emulsions are free of fat clusters.

Although adsorption of protein undoubtedly occurs as a result of the increase in area of the fat phase, there is correspondingly no measurable increase in the viscosity of the emulsion. This may signify perhaps that only an insignificant quantity of protein has been adsorbed. However, it is extremely doubtful whether an increase in viscosity should attend an increase in the quantity of adsorbed protein, primarily because adsorption may be considered to result only in a change in the distribution of suspended material in a suspension in which water is the suspending medium, rather than in a change in the hydrodynamical volume of the suspended material. This conclusion, of course, follows as a result of a change in viewpoint from the consideration of the medium containing the ingredients

other than fat as the continuous medium to the consideration of water as such. It would also follow if the increase in viscosity associated with the increase in the hydrodynamical volume of the fat phase is considered to be exactly compensated by the decrease in viscosity of the continuous medium due to the removal of protein from this medium.

An increase in the viscosity of an emulsion may attend an increase in the specific area of the dispersed phase because of a quasi-viscous effect due to electrokinetic influences. The modified Einstein equation in which the contribution to the viscosity of the quasi-viscous effect appears, is given by Smoluchowski (3):

$$\frac{\eta}{\eta_0} = \left[1 + 2.5 V \left(1 + \frac{10^{-4} R D^2 \zeta^2}{36 \pi^2 a^2 \eta_0} \right) \right]$$

where D = the dielectric constant,

R = the specific resistance in c.g.s. units,

ζ = the zeta potential in volts,

a = the radius of globule in centimeters, and

η and η_0 = the viscosities in poises of the suspension and of the continuous medium, respectively.

In suspensions containing very small quantities of salt, the specific resistance is sufficiently low to render the quasi-viscous effect negligible. Thus, in the case of milk, the factor 2.5 appearing in equation 3 is multiplied by $1 + 0.0005\zeta^2$ when the approximate values 60 for D , 2×10^{-10} c.g.s. units for R , 2×10^{-4} cm. for a , and 0.01 poises for η_0 are inserted in the equation. Consequently, unless the zeta potential of the fat globules is inordinately high, the quasi-viscous effect and the influence on viscosity of the factors contributing to the effect, particularly the degree of dispersion of the suspended material, may be neglected.

It is reasonable to conclude from the results presented in table 2 and from the discussion pertaining to these results, that the viscosity of a suspension is independent of particle size, and that any deviation from this relationship may be attributed to the amplification of the volume of the suspended material by means of the suspending medium.

In view of the general applicability of equation 2 to emulsions varying both in the degree of dispersion of the fat phase, and in the composition of the continuous medium, and in view of its reducibility for low concentrations of fat to Taylor's theoretical equation, it seems reasonable to assume its applicability not only at the temperature employed in the measurements herein recorded, but at all temperatures, and not only to the suspensions under consideration but to all suspensions of spherical particles.

Obviously, however, these conclusions cannot be construed to apply

without further investigation to emulsions exhibiting marked plastic or elastic properties.

In view of the results obtained, the increase in viscosity usually attending the homogenization of cream and ice cream mixes may now be attributed solely to clustering and, consequently, this increase may serve as a basis for the evaluation of an appropriate index of the extent of clumping. Sharp and Troy (5) have shown that the variation of the rate of rise of fat clusters of indefinite shape in milk, with variations in the mean diameter of the cross-section of these clusters, obeys reasonably well Stokes' law governing the relationship existing between the rate of rise of spherical particles and their diameters. If, accordingly, the fat clusters in cream and ice cream mixes may be considered to behave as aggregates spherical in shape, then equation 2 may be applied to such mixes provided that the significance of V , the volume of fat per unit volume of mix, is extended to include, in addition to the fat volume, the apparent volume of the continuous medium included in the interstices of the fat clusters per unit volume of mix. The evaluation of this volume of continuous medium with the aid of equation 2 necessitates two viscosity measurements—one on the mix under consideration and the other on the continuous medium. The difference between the measured and calculated values of V , divided by the measured value of V , gives the apparent volume of continuous medium associated with the fat clusters per unit volume of dispersed fat; and this quantity may appropriately be designated as a clumping index.

SUMMARY

The viscosity of emulsions containing milk fat does not vary within the limits of experimental error with variations in the degree of dispersion of the fat phase, provided that in these emulsions the actual volume of the fat phase is not measurably amplified by the association with the fat phase of a portion of the continuous medium.

An empirical equation expressing the relationship between the viscosity and the fat content of these emulsions has been obtained. For low concentrations of fat, this equation reduces to that derived by Taylor on the basis of theoretical hydrodynamics, regardless of the composition of the continuous medium, that is, of the medium in which the fat is suspended.

The difference between the hydrodynamical volume of fat, calculated from viscosity data, and the actual volume provides a basis for the calculations of a clumping index applicable to cream and ice cream mixes.

REFERENCES

- (1) Associates of L. A. Rogers: *Fundamentals of Dairy Science*, p. 35. Reinhold Publishing Corporation, New York (1935).
- (2) HENING, J. C., AND DAHLBERG, A. C.: *J. Dairy Sci.* **12**, 129 (1929).
- (3) SMOLUCHOWSKI, M. VON: *Kolloid-Z.* **18**, 190 (1916).
- (4) TAYLOR, G. I.: *Proc. Roy. Soc. London* **138A**, 41 (1932).
- (5) TROY, H. C., AND SHARP, P. F.: *J. Dairy Sci.* **11**, 189 (1928).

ADSORPTION AT CRYSTAL-SOLUTION INTERFACES. VIII

INFLUENCE OF DYES AND OTHER ORGANIC COMPOUNDS ON THE CRYSTAL HABIT OF BARIUM AND LEAD NITRATES¹

PHOEBE PAINE DAVIS AND WESLEY G. FRANCE

Department of Chemistry, The Ohio State University, Columbus, Ohio

Received April 18, 1935

Barium and lead nitrates were selected for study because they are isomorphous and because x-ray evidence indicates the possibility that the three sets of most commonly appearing faces are populated by alternating planes of M^{++} ions in one plane and $(NO_3)^-$ ions in the next. Thus the effect of various dyes on two crystals differing only in the size of their unit cells can be compared. Furthermore, if three different sets of faces exist populated by planes of ions of like charge, one would predict, on the basis of the theory of adsorption and habit modification developed in the previous investigations of this series (1), that certain faces would adsorb given dyes and other faces different dyes, depending in part on the distribution of polar groups in the dye molecule and on the ionic spacing of the faces. It was also thought that the data obtained from these adsorption studies might be of value in determining which of the two forms, pyrite or distorted calcium fluoride, is the more closely approximated in these salts.

EXPERIMENTAL

The lead nitrate and barium nitrate salts were purified by recrystallizing the c.p. material twice from water solution. The solutions in which the crystals were grown were prepared by adding the required volumes of solutions of the foreign materials to the warm saturated salt solutions. The solutions were cooled to room temperature, and the small amount of salt which often crystallized out on cooling was filtered off. Small regular seed crystals were mounted on copper or nichrome wires by means of a tiny spot of sealing wax. The wires were suspended from notched corks fitted into vials containing the various saturated solutions, and the crystals allowed to grow undisturbed for periods ranging from two or three days

¹ Presented in part before the Division of Colloid Chemistry at the Eighty-eighth Meeting of the American Chemical Society, held in Cleveland, Ohio, September, 1934.

TABLE 1

Influence of organic compounds on the crystal habit of barium and lead nitrates

FOREIGN SUBSTANCE	CONCENTRATION IN GRAMS PER CC	DESCRIPTION OF CRYSTAL	
		Ba(NO ₃) ₂	Pb(NO ₃) ₂
Picric acid	0.0005		<i>111</i> , traces 210—pale yellow
Picric acid.	0.001	<i>111</i> ,† traces 100—yellow	<i>210</i> *—yellow
<i>p</i> -Nitrophenol	0.001	<i>111</i> , traces 100 and 210	<i>111</i> , two 100 faces
<i>p</i> -Aminophenol.....	0.001	Insoluble	<i>111</i>
<i>p</i> -Nitroaniline.....	0.001	<i>111</i> , also 100, traces 210	<i>111</i> , also 100, traces 210
Benzamide.	0.001	<i>111</i> , also 100, traces 210	<i>111</i> , also 100, traces 210
Acetanilide.....	0.001	<i>111</i> , also 100	<i>111</i> , traces 100
Hydroquinone	0.001	<i>111</i> , also 100	<i>111</i> , also 100 and 210
Dye No. 4.....	0.00025	<i>210</i> ,—violet	<i>210</i> ,* also 100
Dye No. 4.....	0.001	210,—violet	210,* chocolate
Dye No. 5.....	0.00025	111 and 210	
Dye No. 5.....	0.001		111* and 100—pale pink
Dye No. 6.....	0.00025	210,—pale pink	
Dye No. 6.....	0.001		111* and 210—pale pink
Dye No. 7.....	0.001	<i>111</i> ,—traces 100	<i>111</i> *—pink
Dye No. 8.....	0.001	<i>111</i> ,—traces 100—yellowish	<i>111</i> *—tinted
Dye No. 9.....	0.001	<i>111</i> ,—also 100	Insoluble*
Dyes No. 10–No. 15 ..	0.001	<i>111</i> ,—traces 100	<i>111</i> ,* tinted in some cases
Dye No. 16	0.001	<i>111</i> , and 210, pale green	<i>111</i> ,* bluish
Dyes No. 17–No. 18 ..	0.001	<i>111</i> , traces 100	<i>111</i> ,* tinted
Anthraquinone green.	0.001	<i>111</i> , traces 100—green	Insoluble*
Bismarck brown....	0.0005		<i>111</i> , also 100—tan
Bismarck brown....	0.001	<i>111</i> , traces 100, tan	<i>111</i> ,—brown
Methylene blue.....	0.001	111 and 100—blue on 100	100—blue
Congo red	Insoluble		
Diamine sky blue ..	0.0005	Irregular 111, 100, 210—bluish	
Diamine sky blue.....	0.002		<i>111</i> *.—light blue
Oxamine blue	0.002	210, traces 100, 111—green	<i>111</i> *—blue
{ Methylene blue	0.00002 }		
{ Dye No. 4.....	0.001 }		<i>210</i> —violet
{ Methylene blue.....	0.0001 }	210 and 111	<i>111</i> , also 100
{ Dye No. 4.....	0.0005 }		111 edges and 100 faces blue
{ Methylene blue	0.0005 }		100—purplish blue
{ Dye No. 4.....	0.0005 }		clump

* Results of Starr: Master's thesis, Ohio State University, 1933.

† Italicized faces are predominant ones.

TABLE 1—*Concluded*

FOREIGN SUBSTANCE	CONCENTRATION IN GRAMS PER CC.	DESCRIPTION OF CRYSTAL	
		Ba(NO ₃) ₂	Pb(NO ₃) ₂
{ Methylene blue Dye No. 5..... }	{ 0 00002 0 0005 }	210, light green	
{ Methylene blue Dye No. 6..... }	{ 0 00002 0 0005 }	111 also 100—tan	
{ Methylene blue.... Dye No. 6 . . . }	{ 0 0001 0 0005 }	100—small, muddy brown	
{ Methylene blue . . Dye No. 6 }	{ 0 0005 0 0005 }		100—deep blue, slightly irregular
{ Methylene blue . . . Bismarck brown.. }	{ 0 00002 0 0005 }	111 and 100, pale brown	111—slightly more predominant than 100— 111 mottle gray, 100 mottled blue
{ Methylene blue . . . Bismarck brown . . }	{ 0 00002 0 0005 }		111—mottled brown
{ Methylene blue . . . Bismarck brown . . }	{ 0 0001 0 0005 }	111—traces 100—black	
{ Methylene blue . . Bismarck brown.... }	{ 0 0005 0 0005 }		Little growth; slight darkening of 100 faces

in the case of the lead nitrate to nearly a week in the case of the less soluble barium nitrate.

Table 1 gives the substance present as impurity, its concentration, and the type of crystal formed by both lead nitrate and barium nitrate. The formulas for the series of dyes designated by number have previously been published (1d).

DISCUSSION OF RESULTS

Crystal structure

Considerable doubt still exists concerning the crystal structure of the isomorphous nitrates of barium and lead. Certain crystallographic evidence (2) leads to the assignment of an isometric tetrahedral (T^4) symmetry. On the other hand certain other facts, including evidence from x-ray studies (4, 5), indicate a pyritohedral (T_h^6) symmetry. Assuming T_h^6 as correct, an early estimation of the parameters of barium nitrate led to the conclusion that the structure is a distorted calcium fluoride grouping, while a later determination of parameters based on powder photographs

indicates a pyrite (FeS_2) arrangement. Wyckoff (5) states that, "Since the positions developed from powder data do not give planar nitrate groups or interatomic distances that agree with those in NaNO_3 , additional experiments are to be desired."

If the structure is a pyrite arrangement (which may be most simply considered as a sodium chloride grouping of iron and pairs of sulfur atoms), it is easily seen that the 111 faces have alternating planes of M^{++} in one plane and $(\text{NO}_3)^-$ in the next, and that the 110 and 210 faces both possess a checkerboard arrangement of the above ions but have different interionic distances. If, on the other hand, the structure is a distorted calcium fluoride grouping, the 110 face has alternating rows of positive and negative ions, while the 111, 100, and 210 faces all consist of alternating planes of M^{++} and $(\text{NO}_3)^-$ with varying interionic distances.

While neither structure can explain perfectly the habit assumed by crystals of lead and of barium nitrates grown either from pure solution or from solutions containing foreign material, the evidence obtained in this study shows that the distorted calcium fluoride grouping comes much nearer to fitting the experimental results.

Pure crystals of both lead nitrate and barium nitrate show 111 planes predominating, usually accompanied by very small 100 planes and sometimes by other forms, especially the 210. The results of this study show that foreign substances may be adsorbed on the 111, 100, and 210 faces of these salts.

If Spangenberg's (3) theory is correct, that those faces which are populated by like ions grow most rapidly and hence tend to disappear the soonest, while faces populated by unlike ions grow more slowly and hence become the principal forms, it is seen that a pyrite grouping is immediately ruled out. If this structure were the correct one, the 111 faces, populated by like ions, would grow most rapidly and tend to disappear, while the 100 and 210 faces would grow more slowly and become the predominant forms. Also, according to the theory of modification of crystal habit by foreign substances developed in the earlier investigations of this series (1), impurities should be adsorbed at those faces having the stronger fields of force, in this case the 111. Actually, however, dyes have been observed to be adsorbed at the 210 and 100 faces as well as at the 111 face.

If, on the other hand, the distorted calcium fluoride grouping is taken as the unit cell, the 100, 111, and 210 faces, all populated by alternate planes of like ions, would have strong electrical fields and hence rapid growth rates. But, owing to the different interionic spacings, these faces would all have different rates of perpendicular displacement, and therefore varying degrees of prominence on the crystal. Also, it is to be expected that dye would be adsorbed, if at all, on one or more of these three faces,

which is what actually occurs. One discrepancy, however, exists, namely, the fact that the 110 face, with alternate rows of positive and negative ions and hence with a relatively slow growth rate, does not appear on the pure crystal. This difficulty is no doubt less serious than it at first appears to be, since the slight distortion from the true calcium fluoride grouping which is known to exist may be sufficient to account for the failure of the 110 face to appear. Likewise the apparent lack of agreement between the external and internal forms based on crystallographic and x-ray evidence (2) may also be due to this distortion of the calcium fluoride grouping.

Habit modification

An examination of table 1 shows that in general the influence of the simple organic compounds and also of the dyes used is similar for both lead and barium nitrates. This similarity, however, does not hold in all cases. For example, dyes No. 5 and No. 16 and oxamine blue favor the 210 faces of barium nitrate but not of lead nitrate with the concentrations used; again, while methylene blue produces similar modifications with both salts, a given concentration produces a much greater effect on lead nitrate than on barium nitrate. This general but not complete similarity in behavior is in accord with the theory of habit modification suggested previously (1). It is to be expected from this theory that adsorption would occur on corresponding faces of salts having similar structures (since these faces would have similar force fields), but that the actual foreign substances adsorbed at a given face might not be the same in the two crystals, owing to their different interionic distances. This is borne out by the experimental data.

It is also interesting to note that in some instances only one set of faces adsorbs dye, while in others more than one set is colored. If the distorted calcium fluoride structure is accepted as correct, the 111, 100, and 210 faces are all populated by planes of like ions, so that it might be expected that a given dye would be adsorbed on one, two, or even three of these faces, depending on whether the nature and position of its polar groups were such as to fit the interionic spacings on one, two, or three of the faces. Thus if the structure of the foreign molecule were such that it could be adsorbed on both the 111 and 210 faces, but slightly more on the 210, then, as in the case of picric acid and lead nitrate, a greater retardation of the growth rate of the 210 than of the 111 faces would be expected, with the resulting appearance of both faces colored yellow at low picric acid concentrations and the disappearance of the 111 faces at higher concentrations. In the case of methylene blue, which is adsorbed only on the 100 faces of lead nitrate, or of Bismarck brown, which colors only the 111 faces, it follows that a kind and distribution of polar groups probably exists in

these dyes such that the former fits only into the ionic spacing of the 100 face, and the latter only into that of the 111.

Mixed dyes

The influence of a mixture of two dyes on crystal habit provides an interesting problem which is worthy of considerably more study. For the most part, the mixed dyes used in this study exerted an approximately additive effect. In all cases methylene blue was one of the dyes used; the second dye was one which favored either the 111 or the 210 faces. Where the concentration of methylene blue was very low (0.00002 g. per cubic centimeter), the effect of the second dye usually predominated; with a higher concentration of methylene blue the effect of this dye masked any influence the second dye might have had, or the sets of faces favored by each dye appeared. When fairly high concentrations of both dyes were used, growth was greatly inhibited.

In two cases where mixed dyes were used, once with Bismarck brown and once with dye No. 4, the effect was not additive. The absence of the expected additive results in this case indicates the need for further study.

Powder photographs

X-ray powder photographs of the opaque crystals of lead nitrate obtained from water solution, of the clear crystals formed in a solution containing a little nitric acid, and of the deep blue crystals colored by methylene blue, all indicated that the lattice constants are the same for each of the three types of crystals.

SUMMARY

1. The habit assumed by crystals of lead nitrate and of barium nitrate grown both from pure solutions and from solutions containing foreign materials indicates that of the two possible structures—pyrite and distorted calcium fluoride—suggested by x-ray and crystallographic evidence for these crystals, the latter is most closely approximated.

2. The results obtained on the adsorption of foreign material by growing crystals of lead and barium nitrates furnishes further evidence in favor of the theory previously suggested, in the earlier papers of this series of investigations, to account for adsorption and habit modification.

3. The effect on the crystal habit of barium and of lead nitrates of a mixture of two dyes, both of which produce a modification when present alone, is generally, but not always, approximately an additive one.

REFERENCES

- (1) (a) McBurney and France: J. Am. Chem. Soc. **46**, 540 (1924).
- (b) Eckert and France: J. Am. Ceram. Soc. **10**, 579 (1927).

- (1) (c) KEENAN AND FRANCE: *ibid.* **10**, 821 (1927).
- (d) FRANCE: Colloid Symposium Monograph **7**, 59 (1930).
- (e) LASH AND FRANCE: *J. Phys. Chem.* **34**, 724 (1930).
- (f) FOOTE, BLAKE, AND FRANCE: *ibid.* **34**, 2236 (1930).
- (g) WEINLAND AND FRANCE: *ibid.* **36**, 2832 (1932).
- (h) PAINE AND FRANCE: *ibid.* **39**, 425 (1935).
- (2) JAEGER AND VAN MELLE: *Proc. Acad. Sci. Amsterdam* **31**, 651-5 (1928).
- (3) SPANGENBERG: *Z. Krist.* **59**, 375, 383 (1924); **61**, 189 (1925).
- (4) VEGARD AND BILBERG: *Skrifter Norske Videnskaps-Akad. Oslo. I. Mat. Naturv. Klasse*, No. **12**, 1-22 (1931).
- (5) WYCKOFF: *The Structure of Crystals*, 2nd edition, p. 280. The Chemical Catalog Co., Inc., New York (1931).

OBSERVATIONS ON POLYMORPHISM¹

H. E. PHIPPS² AND J. H. REEDY

Department of Chemistry, University of Illinois, Urbana, Illinois

Received May 2, 1935

I. THE DETERMINATION OF TRANSITION POINTS BY MEANS OF THE DIPPING REFRACTOMETER

The determination of enantiotropic transition points is generally based on one of two methods: first, the study of properties which are different for each crystalline form, as specific heat, specific volume, specific resistance, etc.; second, the study of properties which become identical at the transition point, such as solubility, electrode potential, properties of saturated solutions, etc. Tammann (26) barely mentions the second method because of the difficulties involved in determinations of this nature. However, when the differences in the physical properties of the two forms are very small and the change from one form to the other occurs slowly, the second group of methods is the more accurate, provided chemically and physically pure enantiomorphs can be prepared. The specific properties can be determined over definite ranges of temperature on both sides of the transition point, so that little or no extrapolation is necessary. The solubility method is an excellent one in such cases, but it is time-consuming and difficult. Dunstan and Langton (7) tried to avoid these difficulties by plotting the viscosities of saturated solutions against temperatures. However, there are many possibilities for error in the procedure and their results were not highly accurate. Cohen (5) has determined the conductivities of saturated solutions on both sides of the transition point. This method is very accurate, but it involves the transfer of a saturated solution to a conductivity cell, or else the use of a cell in which the solution can be stirred.

We propose the following method, which is free from the difficulties found in other procedures. The refractive indices of the saturated solutions of the two enantiomorphs are determined over the required tempera-

¹ This article is based upon part of a thesis submitted by H. E. Phipps to the Faculty of the Graduate School of the University of Illinois in partial fulfillment of the requirements for the degree of Doctor of Philosophy, May, 1931, and was presented at the Eighty-first Meeting of the American Chemical Society, held in Indianapolis, April, 1931.

² Present address: Department of Physical Science, Eastern Illinois State Teachers' College, Charleston, Illinois.

ture range by means of a dipping refractometer. The data are then plotted or treated mathematically, and the point of intersection of the two curves determined. This method is superior to the ordinary solubility method because (1) the readings may be taken at any temperature within the range of the instrument in less than one minute, (2) any slight change in concentration is easily and quickly detected, (3) readings are taken while the liquid is in intimate contact with the suspended solid, and (4) after the apparatus is set up and the determination started, no experimental manipulations are necessary other than reading the scale of the refractometer and the temperature-recording device. The method is limited to the tempera-

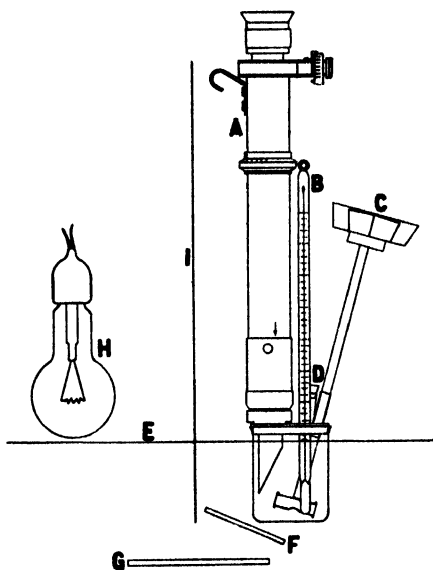


FIG. 1. The apparatus

ture range of the instrument and to solutions which transmit the sodium line. Other types of refractometers might be used to overcome these difficulties.

APPARATUS AND PROCEDURE

The apparatus is shown diagrammatically in figure 1. A is a Bausch and Lomb dipping refractometer equipped with interchangeable prisms. The dipping prism is inserted through a cork which is fitted into the top of a 125-cc. beaker. The thermometer B was graduated to 0.05°C . and had been calibrated by the United States Bureau of Standards. C is a small centrifugal stirrer operated by means of a jet of air. The tube D is added to the apparatus to simplify addition of the solid or removal of

solution from the beaker while a determination is in progress. The beaker and contents were placed in a thermostat which could be regulated to 0.01°C. of the desired temperature. The water level in the thermostat is shown by the line E. The light was supplied by a Mazda bulb H and was reflected by the mirror G. The ground glass F was placed so as to give the maximum sharpness to the division line in the refractometer eye-piece. I was a shield to stop extraneous light from reaching the eye of the observer.

Temperature and refractive index measurements were made simultaneously, and in order to be certain that the solution was saturated and that the material was not changing from one physical modification to another, repeated readings were taken at the same temperature. Any change taking place in the solution could be followed easily by the refractive index measurements. When the readings of temperature and refractive index remained constant for an interval of 30 minutes, it was assumed that equilibrium had been established. In some cases as much as twenty-four hours were necessary for constant readings to be obtained. In order to be doubly certain that the solution was saturated, the final temperature was approached from both directions.

Determination of the transition temperatures of sodium sulfate and sodium carbonate as a check on the method

The method was checked experimentally by determining the transition temperature of the hydrates of sodium sulfate. Richards and his coworkers (24), and Dickinson and Mueller (6) had previously determined the temperature of the transition $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} \rightleftharpoons \text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}$ to be 32.383°C. and 32.384°C., respectively, the latter value being more generally accepted.

The starting material was c.p. sodium sulfate. It was recrystallized four times, completely dissolved, filtered, and recrystallized again. The mother liquor was drained off and the crystals placed on a suction filter and washed with a little cold water. When nearly dry, they were crushed in a mortar and stored in a tightly stoppered bottle until wanted. During the actual determination, enough crystals were always present to cause a slight turbidity in the solution. Four series of determinations were made with sodium sulfate, representative results of which are graphically shown in figure 2. Each scale reading recorded is the average of three or more separate readings. The readings very rarely differed from the mean by more than 0.01 scale division. The thermometer readings were corrected for emergent stem and calibration errors.

The transition point was found to be 32.36°C. in every case. Using the hydrated salt, the saturation point was quickly reached with either rising or falling temperatures, and the results were easily reproduced. This was not the case with the anhydrous material. It was necessary to stir the

solution for a considerable period of time in order to obtain equilibrium conditions with falling temperature.

Since the transition point was found to be 0.02°C . lower than the accepted value, the transition temperature was determined by the method recommended by Dickinson and Mueller (6), in which the crushed decahydrate was placed in a tube in cold water until recrystallization commenced. The tube was then jacketed and placed in a thermostat. The value obtained by this method was identical with the first, viz., 32.36°C . This probably means that the thermometer reads 0.02°C . low at this temperature. Since it was calibrated to 0.05°C ., this difference is not

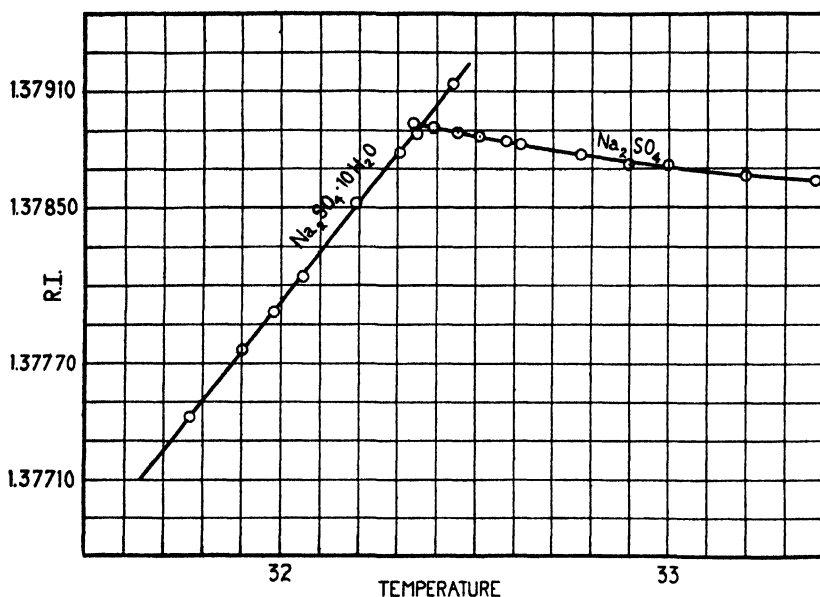


FIG. 2. Transition point of sodium sulfate

outside the limits of experimental error, especially since there was no ice point marked upon it.

A second check on the dipping refractometer method for determining transition points was made by checking the two following well-known points: $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O} \rightleftharpoons \text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O} + 3\text{H}_2\text{O}$, and $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O} \rightleftharpoons \text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O} + 6\text{H}_2\text{O}$. Using highly purified material, Richards and Fiske (23) found the transition temperature of the first to be 32.017°C . Other determinations were as follows: 31.8°C . by Eppler (8), 31.85°C . by Ketner (17), 32.00°C . by Wells and McAdam (29), and 31.85°C . by Usanovich (27). Wells and McAdam seem to be the only ones who have determined the heptahydrate-monohydrate transition with great care,

obtaining 35.37°C. as the best value. Epple gave the temperature as 35.1°C., while Richards and Churchill recorded it as 35.2°C. Wells and McAdam also determined the temperature of the metastable decahydrate-monohydrate transition and found it to be 32.96°C.

The starting material used in this investigation was a high grade of c.p. sodium carbonate. It was purified in the same manner as the sodium sulfate, except that it was recrystallized ten times instead of five, the final recrystallization being carried out just before the material was used. Richards and Fiske found that if the crystals stood for some time before they were used, they took up carbon dioxide from the air and were partially

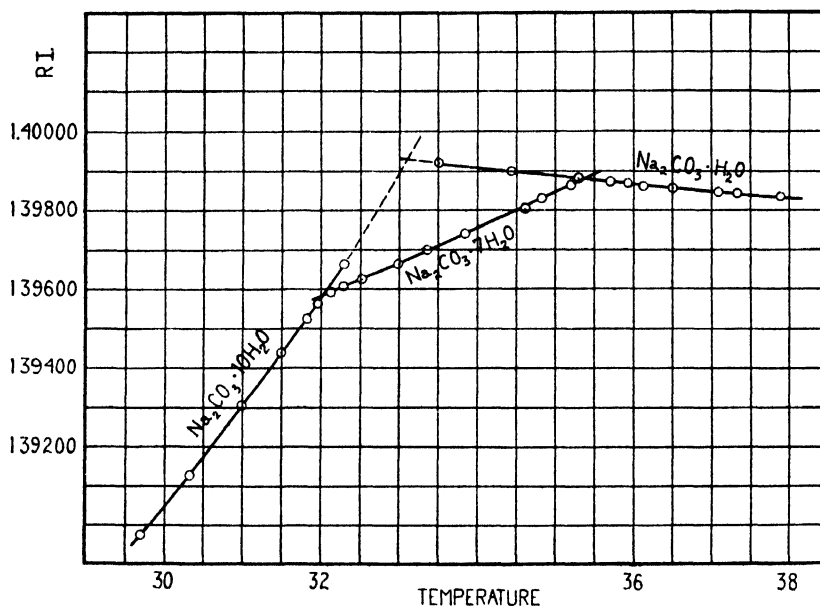


FIG. 3. Transition point of sodium carbonate

converted to the bicarbonate. They carried out their final recrystallization in platinum dishes, in order to avoid contamination by silica from the glassware. Since this raised the transition point only a few thousandths of a degree, and since Pyrex dishes were used throughout the present work, this was thought unnecessary.

Two determinations of the transition points of sodium carbonate were made. No difficulty was found in obtaining perfect checks at the various temperatures, as in the case of the anhydrous sodium sulfate. Equilibrium was quickly established with either rising or falling temperatures. The results are shown in figure 3. From these data, the decahydrate-heptahydrate transition temperature was found to be 32.02°C., the hepta-

hydrate-monohydrate temperature was $35.34^{\circ}\text{C}.$, and, by extrapolation, the metastable decahydrate-monohydrate temperature was $33.1^{\circ}\text{C}.$ The limits of error were of the order of 0.02° , 0.02° , and $0.1^{\circ}\text{C}.$, respectively. These results show that this method can be used to determine transition points with considerable accuracy.

II. THE CRYSTALLINE FORM OF AMMONIUM NITRATE III

During the course of some unpublished work on the transition temperature of ammonium nitrate III \rightleftharpoons ammonium nitrate IV (also designated as γ and β), it was found that there was no general agreement in the various references in chemical literature as to whether ammonium nitrate III is orthorhombic or monoclinic.

Ammonium nitrate was first reported to be dimorphic by Frankenheim (10) in 1854. Later, Lehmann (19) showed that there are five distinct forms stable at atmospheric pressure, and Bridgman (2) has found a sixth form stable only at high pressures. In reporting his work, Frankenheim placed the form stable at room temperature (NH_4NO_3 IV) in the rhombic system, but was undecided as to what system NH_4NO_3 III belonged to. Marignac (20), von Lang (30), and others have studied the crystalline properties of ammonium nitrate, but seem to have worked with form IV exclusively. Lehmann placed both forms in the rhombic system, and reported that IV has a higher birefringence than III. He designated them as α -rhombic and β -rhombic, respectively. In 1905 Wallerant (28) reported the crystals to be "monocliniques quasiquadratiques." He stated that if Lehmann had examined form III with oblique polarized light, he would have found that it belonged to the monoclinic rather than the rhombic system. However, Wallerant worked with the solidified melts of modification III which had been stabilized by the addition of potassium nitrate. Caillart (3) studied the solubility curves for mixtures of ammonium and potassium nitrates, and found that crystals separating from different compositions have different crystal structures, as follows: crystals containing less than 17.2 mole per cent of ammonium nitrate show the regular rhombic structure of potassium nitrate; crystals containing 55 to 94.5 mole per cent of ammonium nitrate are monoclinic (cf. Wallerant's crystals); and crystals containing 98 to 100 mole per cent ammonium nitrate are rhombic (modification IV). As Jänecke (14) has pointed out, Wallerant was probably working with a solid solution of potassium nitrate in ammonium nitrate. It is also possible that equilibrium had not been established in the crystals on the microscope slide. In this way it is easy to explain how he may have assigned the crystals to the wrong system. Flörke (9) referred to both forms as belonging to the rhombic system. Bowen (1) reported that modification III was monoclinic or orthorhombic with a moderately high birefringence, but not as high as that of form IV. Since the completion

of our work (1931), Hendricks, Posnjak, and Kracek (12), from an x-ray examination, have come to the conclusion that form III is probably orthorhombic.

Experimental

The ammonium nitrate used in this work was of c.p. grade, recrystallized three times.

The first experiments were made with crystals which had been melted and allowed to cool slowly on the stage of a petrographic microscope. The three transitions were not always observed with this pure material; sometimes only two were found. On the other hand, if crystals which had not been recrystallized were used, three transitions were always found, either on heating or cooling. The failure to find the IV→III transition was at first thought to be due to the supercooling of modification III, a behavior not uncommon in very pure substances. Very careful examination showed that form III was entirely absent, and that the transition progressed in the order I→II→IV on cooling, and IV→II→I on heating. This is in agreement with the work of Bowen, who found that a metastable region between II and IV often develops upon cooling a melt of pure salt. He also found that, in some ways, the II→IV transition is more easily reversed than with the more stable forms. However, if modification III was formed at any time, the direct transition II→IV could not be observed unless the material was melted or else completely converted to modification I. The difference between forms III and IV is shown in the microphotograph (figure 4). The perfect crystals of form III obtained from melts were always rhombic. However, since this is not the best procedure for determining a crystal system (vide Chamot and Mason (4)), a second series of experiments was undertaken.

An electrically heated hot stage was devised, and adjusted to 37°C. by means of a thermostat. A drop of a hot concentrated solution of ammonium nitrate was placed on the slide, covered with a cover glass, and allowed to crystallize slowly. When equilibrium between the crystals and the mother liquor was reached, a coating of collodion was placed around the edge of the cover glass to prevent creeping and evaporation. This had no detrimental effect, and made a more leisurely and thorough examination possible. At least two hundred crystals were examined in this way. Many were so oriented as to give a good biaxial interference figure with convergent polarized light. All the crystals examined showed parallel extinction, and were long needles or diamond-shaped plates. If the temperature was allowed to fall below 32°C. and remain there for a few hours, these needles and plates changed in appearance, and showed the presence of many smaller crystals which also belonged to the rhombic system, but were more highly birefringent. If the temperature was raised to 37°C.,

the change took place in the opposite direction. The large crystals again appeared perfectly homogeneous, only occasionally showing cleavage cracks or crystal boundaries where there were none before.

Since it was possible that the crystals examined might have been so oriented that only two crystallographic axes were examined for the extinc-



FIG. 4. Microphotographs of ammonium nitrate III and IV. a, ammonium nitrate III; b, ammonium nitrate IV; c, ammonium nitrate IV (black) growing at the expense of ammonium nitrate III (light).

tion angle (vide Johannsen (15)), some large well-formed crystals were grown at 37°C. These were oriented so that the different crystallographic axes were parallel and perpendicular to the optical axis of the microscope. Refractive index measurements indicated that the axes of elasticity coincide with the crystallographic axes. Parallel extinction was found in all

cases, so that there can be no doubt that ammonium nitrate III is orthorhombic.

III. THE TRANSITION POINT OF CARBON TETRACHLORIDE

The transition temperature of carbon tetrachloride has been previously determined by several investigators. Goldschmidt (11) reported it as $-45 \pm 5^\circ\text{C}$., Latimer (18) -48.5°C ., McCullough and Phipps (21) $-48.54 \pm 0.02^\circ\text{C}$., and Skau and Meier (25) $-47.55 \pm 0.12^\circ\text{C}$.. Since the last value is a degree higher than that previously found by the junior author, a redetermination was undertaken to locate the cause of the difference. Since this work was completed (1931), Johnston and Long (16) have reported a value of $-47.66 \pm 0.05^\circ\text{C}$., and have proposed that it be used as a fixed point in thermometry.

Experimental

The carbon tetrachloride used in this work was obtained through the United States Bureau of Standards from Dr. Timmermans, who gave its

TABLE 1
Transition points

SUBSTANCE	PHENOMENON	HEATING	COOLING	TIMMER- MANS' VALUES
		$^\circ\text{C}$.	$^\circ\text{C}$.	$^\circ\text{C}$
CCl_4	Freezing point	$-22.83 \pm .01$	$-22.84 \pm .01$	-22.85
CCl_4	Transition point	-47.46	-47.87	
$\text{C}_6\text{H}_5\text{Cl}$	Freezing point	$-45.32 \pm .01$	$-45.35 \pm .01$	-45.35

freezing point as -22.85°C .. A sample of chlorobenzene with a freezing point of -45.35°C .. was obtained from the same source, and served admirably as a check on the thermocouple calibration.

The thermocouple used in this work was made of No. 30 constantan and No. 36 copper wire. There were five junctions, each of which was placed in a very thin-walled capillary tube, containing a drop of light oil to improve the thermal contact. The thermocouple was tested for inhomogeneities by interchanging the ends in steam and ice and in ice and liquid air. No differences in the readings were detected under these extreme conditions. The couple was calibrated at the steam point, the ice point, the freezing point of mercury (-38.87°C .) (13), and the sublimation point of carbon dioxide (78.2°C .) Of these points, the last is the least reliable. A carefully calibrated type K potentiometer and type HS galvanometer were used to determine the E.M.F. of the thermocouple.

A 10-g. sample was placed in a specially constructed Dewar tube, so arranged that the air content between the walls could be varied. The tube

was placed in a small cryostat, the temperature of which could be changed slowly. Besides the thermocouple, the tube also contained a small stirrer.

The third and fourth columns of table 1 show the values obtained for the freezing points of carbon tetrachloride and chlorobenzene, and for the transition point of carbon tetrachloride. Both the heating and cooling curves were used in obtaining these values. For comparison, Timmermans' values are placed in the last column.

A temperature gradient of 0.1°C. per minute was used. A more rapid change (e.g., 0.3°C. per minute) did not change the freezing points, but the transition point was not sharp. Evidently the velocity of the reaction is not sufficient to maintain a constant temperature.

In a later run, a slight amount of impurity was accidentally introduced into the carbon tetrachloride, resulting in a lowering of the freezing point of 0.1°C. and of the transition point of 0.27°C. Timmermans has stated that the freezing point of carbon tetrachloride is very sensitive to minute traces of impurities. Evidently the transition point is affected to a much greater degree. In the determination made by the junior author in 1928, the material was not as pure as might be desired, as shown by the fact that its freezing point was -22.95°C. , and there was no evidence of supercooling at the transition point. With very pure carbon tetrachloride, supercooling of 2 to 3°C. was extremely difficult to prevent. The results in this earlier work were based entirely upon cooling curves, and the rate of temperature change was approximately $0.2\text{--}0.3^{\circ}\text{C.}$ per minute. These facts explain why the first result was 0.9°C. lower than the present value, which is in practical agreement with that of Johnston and Long.

In their paper on the transition point of carbon tetrachloride, Skau and Meier (25) make the following statement: "It was found that the heating curve value was fairly reproducible, but that the value obtained from cooling curves varied from -47.67 to -47.99° , depending on the conditions; that is, on the degree of supercooling and on the rate of cooling. In such cases as this, where one cannot establish equilibrium by stirring, due to the fact that the change takes place in the solid state, it is of course to be expected that the proper degree of supercooling before the transition takes place is very important. Our best curves for this point were obtained with a supercooling of 3 to 4° , the rate of cooling being about 0.3° per minute."

These authors cited Nernst's discussion of the danger of supercooling too little or too much in cryoscopic determinations in dilute solutions (22). On the other hand, the conditions prevailing in dilute solutions may be vastly different from those prevailing in the enantiotropic transition of a pure substance. Tammann (26) states that supercooling and superheating should be avoided as much as possible, because they change the form of the curves at the point of halt. This makes the true equilibrium very difficult to obtain. Consequently excess supercooling should be avoided.

SUMMARY

1. A new method for determining the transition temperature of soluble substances by means of the dipping refractometer has been devised. This method is especially useful in cases where the velocity of transition is so small that ordinary methods are inaccurate. It is much simpler and faster than the solubility method and just as exact.

2. Examination of ammonium nitrate III by means of a petrographic microscope indicates that it is orthorhombic.

3. The transition point of carbon tetrachloride has been redetermined as $-47.66 \pm 0.2^{\circ}\text{C}$. from heating and cooling curve measurements. This temperature is affected by impurities nearly three times as much as the melting point, and is not recommended as a fixed point in thermometry.

REFERENCES

- (1) BOWEN, N. L.: *J. Phys. Chem.* **30**, 721, 726 (1926).
- (2) BRIDGMAN, P. W.: *Proc. Am. Acad. Arts Sci.* **51**, 581 (1916).
- (3) CAILLART, M.: *Bull. soc. franç. minéral.* **41**, 21 (1918).
- (4) CHAMOT, E. M., AND MASON, C. W.: *Handbook of Chemical Microscopy*, Vol. I, pp. 354-6. John Wiley and Sons, New York (1930).
- (5) COHEN, ERNST: *Z. physik. Chem.* **31**, 164 (1899).
- (6) DICKINSON, H. C., AND MUELLER, E. F.: *Bur. Standards Bull.* **3**, 641 (1907).
- (7) DUNSTAN, A. E., AND LANGTON, HAROLD: *J. Chem. Soc.* **101**, 418 (1912).
- (8) EPPLE: *Inaugural dissertation*, Heidelberg, 1899.
- (9) FLÜRKE, W.: *Z. physik. chem. Unterricht* **40**, 71 (1927).
- (10) FRANKENHEIM: *Pogg. Ann.* **93**, 14 (1854).
- (11) GOLDSCHMIDT, V. M.: *Z. Krist.* **51**, 26 (1913).
- (12) HENDRICKS, S. B., POSNJAK, E., AND KRACEK, F. C.: *J. Am. Chem. Soc.* **54**, 2766 (1932).
- (13) *International Critical Tables*, Vol. I, pp. 54-8. McGraw-Hill Book Co., New York (1926).
- (14) JÄNECKE, E.: *Z. angew. Chem.* **41**, 916 (1928).
- (15) JOHANNSEN, ALBERT: *Manual of Petrographic Methods*, 1st edition, pp. 12-4. McGraw-Hill Book Co., New York (1908).
- (16) JOHNSTON, H. L., AND LONG, E. A.: *J. Am. Chem. Soc.* **56**, 31 (1934).
- (17) KETNER, C. H.: *Z. physik. Chem.* **39**, 642 (1902).
- (18) LATIMER, W. M.: *J. Am. Chem. Soc.* **44**, 90 (1922).
- (19) LEHMANN, O.: *Z. Krist.* **1**, 97 (1877); *Molekularphysik*, pp. 153-61. Engelmann, Leipzig (1888).
- (20) MARIIGNAC: *Ann. mines* [5] **12**, 22 (1857).
- (21) McCULLOUGH, J. C., AND PHIPPS, H. E.: *J. Am. Chem. Soc.* **50**, 2213 (1928).
- (22) NERNST, W., AND ABEGG, R.: *Z. physik. Chem.* **15**, 681 (1894).
- (23) RICHARDS, T. W., AND FISKE, A. H.: *J. Am. Chem. Soc.* **36**, 485 (1914).
- (24) RICHARDS, T. W., AND COWORKERS: *Am. Acad. Arts Sci.* **34**, 277 (1898-99); **38**, 429 (1902); *Am. J. Sci.* [4] **6**, 201 (1898); *Z. physik. Chem.* **26**, 690 (1898); **28**, 315 (1899); **43**, 471 (1903).
- (25) SKAU, E. L., AND MEIER, H. F.: *J. Am. Chem. Soc.* **51**, 3517 (1929).
- (26) TAMMANN, GUSTAV: *The States of Aggregation*, pp. 123-7. D. Van Nostrand Co., New York (1925).

- (27) USSANOVICH, M.: Z. physik. Chem. **119**, 139 (1926).
- (28) WALLERANT: Bull. soc. franç. minéral. **28**, 311 (1905); **39**, 162 (1916); Compt. rend. **142**, 217 (1906).
- (29) WELLS, R. C., AND McADAM, D. J.: J. Am. Chem. Soc. **29**, 721 (1907).
- (30) VON LANG: Sitzber. Akad. Wiss. Wien Math. naturw. Klasse **31**, 101 (1858).

ADSORPTION ON CHROMITE CATALYSTS

J. C. W. FRAZER AND C. G. ALBERT¹

Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland

Received May 2, 1935

The close relation between the adsorption of gases by solids and contact catalysis is quite generally accepted, and has been much discussed in the literature. In this laboratory the chromites have been thoroughly studied as catalysts for the oxidation of carbon monoxide by Lory (5) and later by Lockwood (4). This suggested that a detailed study of the adsorption by chromite catalysts of carbon monoxide and oxygen, paying particular attention to the so-called "activated adsorption," would not be without interest and value in shedding more light on the question of the relation between adsorption and catalytic activity.

If adsorption does play a major part in contact catalysis, it is certainly this high-temperature variety, with its "energy of activation," which must be considered. For, as Garner pointed out (3), when Taylor (7) described the phenomenon in 1931, he suggested the term "activated adsorption" merely to indicate that the process taking place was one which involved a temperature coefficient, although the fact that it occurs at the temperatures at which the surface under consideration is catalytically active might be construed as indicating that the term might equally well have been used to mean that the adsorbed molecules are in some active state.

Since the surface of the chromite catalyst under consideration is catalytically active for the combination of carbon monoxide and oxygen at temperatures of 100–200°C., its adsorption of both of these gases was studied over this range in temperature, noting particularly the rate at which the adsorption process takes place. The purpose of the investigation was to measure the extent to which the adsorption takes place, and also to obtain sufficient data on its rate to permit the calculation of the energy of activation associated with the process in each case.

APPARATUS

The apparatus used in making these measurements was essentially the same as that described by McKinney (6) and used also by Taylor and

¹ From a dissertation submitted to the Faculty of the Graduate School of the Johns Hopkins University in partial fulfillment of the requirements for the degree of Doctor of Philosophy June, 1935.

Strother (8). Like McKinney's apparatus, it was so designed as to permit the measurement of adsorption at constant pressure, with its rate, and also to measure the adsorption at constant volume in order to plot the isothermals.

The gas buret used in these measurements was graduated in hundredths of a cubic centimeter, and the distance between these graduations was over a millimeter,—large enough so that fractions of a division could be estimated with considerable accuracy. The buret was surrounded by a water jacket through which a constant stream of small bubbles of air was kept flowing in order to insure uniformity of temperature along the length of the buret. A thermometer, graduated in fifths of a degree, was suspended in the water jacket, and the temperature was recorded each time a reading was made.

THE CATALYST

The sample of copper chromite used in the adsorption measurements was the Copper Chromite No. 1 prepared and tested for its efficiency by Lockwood (4). At the conclusion of the adsorption measurements, the

TABLE 1
Efficiency of copper chromite No. 1 after the adsorption measurements

TEMPERATURE	CONVERSION
°C.	per cent
139	40
166	85
181	100

catalyst was again tested, using the same apparatus used by Lockwood. The results obtained were, within a reasonable experimental error, the same as those of Lockwood, which are summarized in table 1.

MATERIALS

The gases used in the adsorption measurements were very carefully purified before being placed in their storage bulbs. Each gas was passed through its purification train for at least an hour, in order to sweep out the air, before being admitted to the system.

EXPERIMENTAL RESULTS

Adsorption of oxygen at constant pressure

The adsorption of oxygen at a pressure of 350 mm. Hg was studied at temperatures covering the range over which the activity of copper chromite as a catalyst for the air oxidation of carbon monoxide varies from prac-

tically no activity at all to 100 per cent conversion of carbon monoxide to carbon dioxide.

In order to make the results at different temperatures comparable, the catalyst was heated, before each run, to 300°C. under 400 mm. Hg of

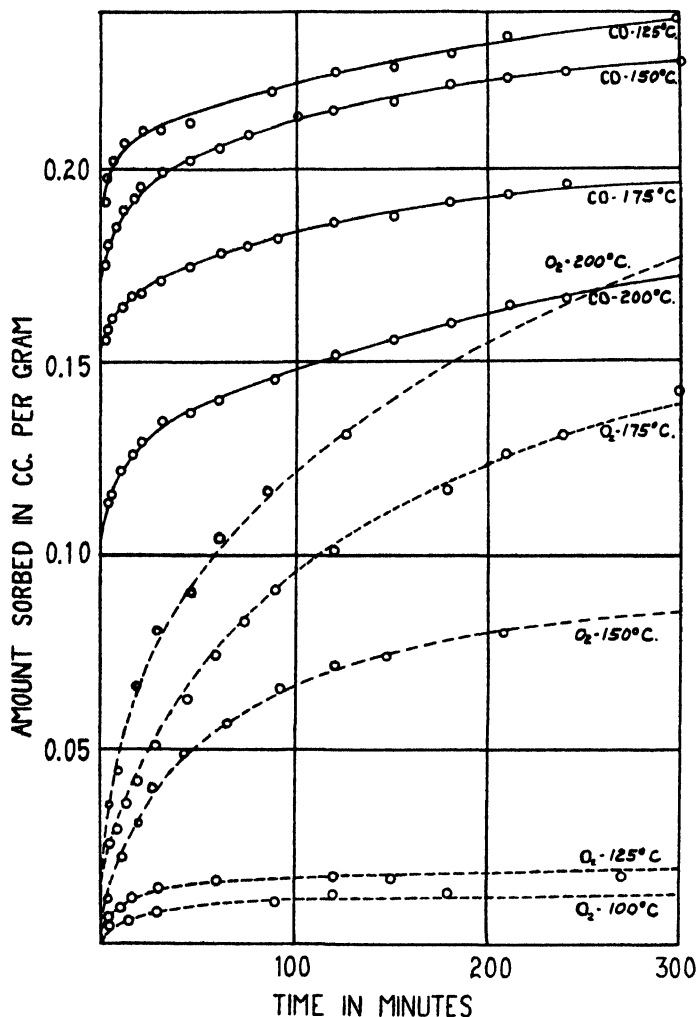


FIG. 1. Adsorption of carbon monoxide and oxygen on copper chromite at 350 mm. of mercury

carbon monoxide, and then thoroughly evacuated. Lory (5) states that any surface chromate formed is reduced by carbon monoxide at 100°C. The treatment given the catalyst, then, should surely prevent any chromate formed during the previous run from interfering with the results. All of

the runs were checked several times, and the curves obtained could be duplicated within about 2 per cent. The data on the adsorption of oxygen are represented graphically in figure 1.

It is evident from the figure that the adsorption of oxygen at these temperatures exhibits the one chief characteristic of activated adsorption to which Taylor called attention,—a rate which, over the temperature range studied, shows a marked increase with increasing temperature. In this

TABLE 2
Activation energies of adsorption of oxygen on copper chromite

AMOUNT ADSORBED	E (IN KG-CAL.)					
	100-125°C.	100-150°C.	125-150°C.	150-175°C.	150-200°C.	175-200°C.
0.00500	15.43					
0.00625	15.78					
0.00750	17.41	16 19	14.79			
0.00875	17.71					
0.01000	19.11	17.50	15.66			
0.01125	20.51					
0.01250	25.51	22 62	18.66			
0.01500	22.04					
0.03				9.59	9 31	8 99
0 04				9.46	9.54	9.63
0.05				10.19	10.29	10.40
0.06				11.76	11.53	11.28
0.07				13.07	12 29	11.41
0.08				16 50	13.79	10.76
0.09					17.19	10.61
0.10						10.89
0.11						10.96
0.12						11.03
0.13						11.61
0.14						12.72
0.15						15.64

case, not only the rate, but also the extent to which the adsorption occurs, increases greatly with rising temperature.

If, at two temperatures T_1 and T_2 , adsorption takes place to the same extent in the time intervals t_1 and t_2 , the energy of activation to be associated with the adsorption process over that temperature interval may be calculated from the equation

$$\ln \frac{t_2}{t_1} = \frac{E}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

Calculating, with this equation, the energy of activation, E , from the

data illustrated in figure 1 on the adsorption of oxygen at constant pressure by copper chromite, we obtain the values for E listed in table 2.

The fact that the activation energies for the lower temperature ranges come out considerably higher than those at somewhat higher temperatures is due to the fact that the calculations at the lower temperatures involve a much more nearly saturated surface, since the total amount of adsorption which takes place at these temperatures is so much less. At the higher temperatures, the energy of activation is rising to similar values as more of the gas is adsorbed.

Adsorption of carbon monoxide at constant pressure

The adsorption of carbon monoxide on copper chromite at a constant pressure of 350 mm. Hg was studied at the same temperatures used in the study of the oxygen adsorption.

A great deal has been written, particularly by Burrage (2), about the importance, when comparing the rates of reaction found in different runs, of being certain that the surface of the absorbent was in the same condition at the start of each run. When each carbon monoxide run was made after simply pumping off the gas from the previous run at the temperature at which the run had been made, the results obtained could not be checked and appeared to be without meaning. Evidently the condition of the catalyst surface at the beginning of a run varied considerably, according to whether the previous run had been made at a temperature higher or lower than that at which the succeeding run was to be made.

It was decided to make a set of runs after giving the catalyst a definite treatment, the same treatment being used before each run. The catalyst was first heated to 275–300°C. for an hour under a definite pressure of carbon monoxide. Then the catalyst was thoroughly degassed, and allowed to cool down to the desired temperature. Runs made in this manner could be checked to within 2 to 5 per cent. A set of data from such runs is shown graphically in figure 1.

These runs, in which the condition of the catalyst surface should have been about the same, indicate that the amount of adsorption is less the greater the temperature. Obviously, it is impossible to apply the formula used before to the data of figure 1 and to calculate energies of activation. It is apparent, however, that the order in which the curves fall is determined by the amount of instantaneous adsorption.

This part of the adsorption has the characteristics of van der Waals adsorption. Benton (1) stated that in most cases the van der Waals adsorption disappeared at about 200°C. above the boiling point of the gas. However, he found a type of adsorption which showed the speed characteristic of the van der Waals adsorption with carbon monoxide on copper at 110°C., while the boiling point of carbon monoxide is -192°C . The

van der Waals adsorption in the case of carbon monoxide on copper chromite appears to be prominent even at a temperature nearly 400°C . above the boiling point of the carbon monoxide, as is shown by the 0.11 cc. per gram adsorbed instantaneously at 200°C . A brief run was made at 300°C ., and the 1-minute reading at this temperature, in cc. per gram, was 0.03, the curve starting out similarly to those for oxygen at the lower temperatures. This would indicate that finally, 500°C . above the boiling point of the carbon monoxide, the van der Waals adsorption is disappearing from the picture.

If we take the 1-minute reading for each of the carbon monoxide runs, whatever it may be, as zero, and plot the amount adsorbed over and above this fixed quantity against time, curves like those in figure 2 are obtained.

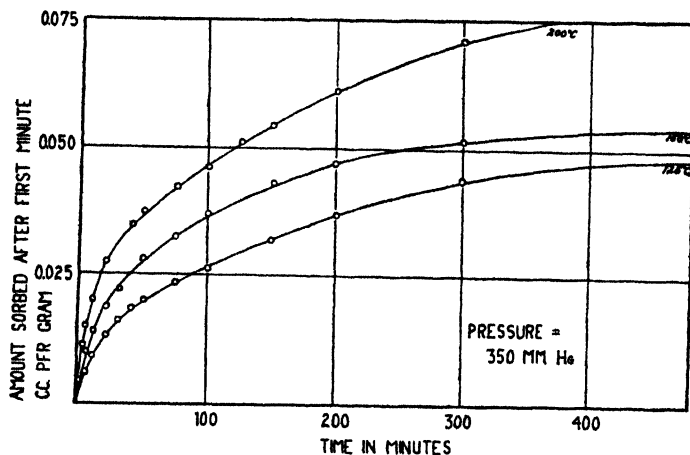


FIG. 2. Activated adsorption of carbon monoxide on copper chromite

These curves are similar to those for oxygen, and are suitable for the calculation of energies of activation.

Since the amounts adsorbed used in plotting the original adsorption versus time curves of figure 1 are obtained by subtracting one experimental value from another nearly the same size, the percentage error in the reading is greatly multiplied by the time the adsorption curves are obtained. The final curves, those of figure 2, are obtained by repeating the process of subtracting one value from another very nearly the same size. Thus the original numbers (the volumes read on the gas buret) have now shrunk to new values numerically only about one-fiftieth of the size of the original ones, and it is to be expected that as a consequence of this the percentage errors will have grown to large proportions.

Nevertheless, it is possible to take these last curves of figure 2 and to calculate from them fairly consistent energies of activation, although the

agreement is quite naturally not nearly as good as in the case of the adsorption of oxygen at constant pressure. Some of the calculations of energies of activation are summarized in table 3.

The rapidity with which a considerable amount of carbon monoxide is adsorbed on the chromite suggested that perhaps something approximating a monomolecular layer is formed at once, and that the "activated" adsorption consists of building up a thicker layer.

TABLE 3
Energies of activation: carbon monoxide on copper chromite

AMOUNT ADSORBED	E (IN KG-CAL.)		
	125-150°C	125-200°C	150-200°C.
0.0100	8.17		
0.0125	7.92		
0.0150	9.34		
0.0175	10.11		
0.0200	11.06	8.61	7.16
0.0225	11.29	8.64	7.07
0.0250	11.74	8.45	6.49
0.0275	11.38	8.42	6.67
0.0300	10.42	8.28	7.01
0.0325	9.70	7.83	6.71

TABLE 4
Carbon monoxide adsorption in the first minute

TEMPERATURE	ADSORPTION
°C.	atoms per gram
100	5.54×10^{18}
125	5.26×10^{18}
150	4.75×10^{18}
175	4.16×10^{18}
200	2.76×10^{18}

Lory (5) studied the amount of chromate that could be leached off samples of various chromites with water, after the chromites had been heated in the air to form a surface layer of the chromate. From the data which he obtained in this manner, he calculated the number of chromium atoms on the surface of the catalyst. For copper chromite he obtained the value 4.11×10^{18} atoms of chromium on the surface for each gram of the catalyst.

The sample of copper chromite used in these measurements was prepared by following Lory's method to the smallest detail, and may be assumed to have approximately the same number of surface chromium atoms. If we assume that the adsorption takes place on the chromium atoms, then a

monomolecular layer must be considered as one molecule of carbon monoxide to each surface chromium atom, or about 4.11×10^{18} atoms per gram. The observed amounts of carbon monoxide adsorption in the first minute, converted from cubic centimeters per gram to atoms per gram are given in table 4. Obviously, the amount of this rapid adsorption is, at the temperatures studied, of the same order of magnitude as that required to form a monomolecular layer on the surface of the catalyst.

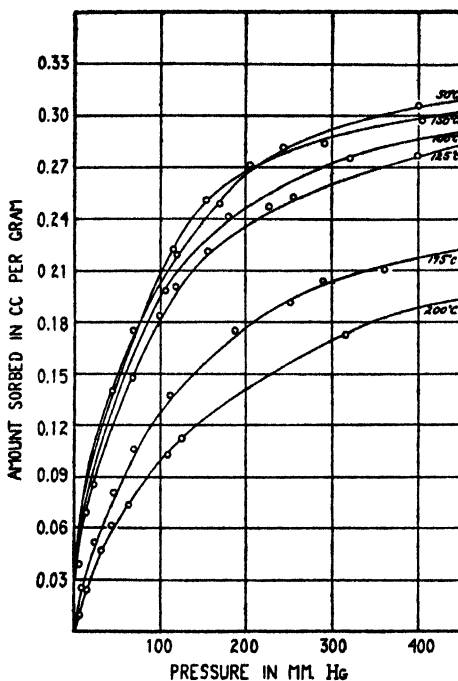


Fig. 3. Adsorption of carbon monoxide on copper chromite at constant volume

Adsorption of carbon monoxide at constant volume

The different character of the adsorption versus time curves for carbon monoxide, as compared with those for oxygen, suggested that the processes taking place were not of the same nature.

In order to obtain a better understanding of the question of the adsorption of carbon monoxide, it was considered worth while to obtain the data necessary to plot the isotherms for the adsorption of carbon monoxide,—the total adsorption of all kinds when equilibrium had been reached. With this in mind, constant volume runs were made at seven temperatures, covering the entire range where the catalyst is active. The data thus obtained are shown graphically in figure 3.

DISCUSSION

The adsorption of oxygen by copper chromite appears to be a straightforward process. It seems probable that it is simply a chemical reaction, that of surface chromate formation. At the temperature range over which the adsorption was studied, which is the important range as regards catalysis, the activated adsorption is the only process taking place, so that there are no complications introduced by concurrent reactions.

The case of the adsorption of carbon monoxide on copper chromite is not so simple. Two adsorption processes combine to give the observed results, and it is only by separating the two and considering each one individually that we can obtain any understanding of either one. The curves

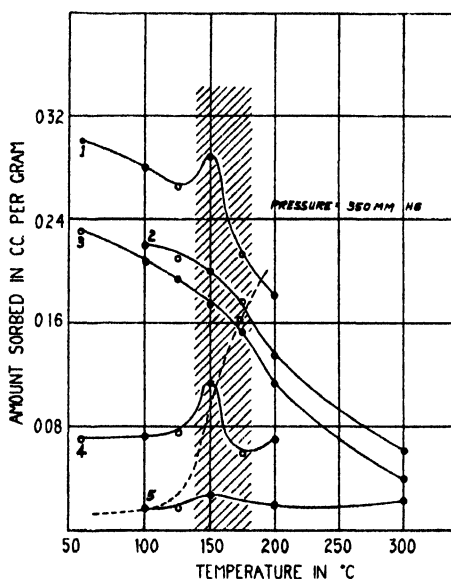


FIG. 4. Summary of carbon monoxide adsorption

of figure 4 represent both the sum of the van der Waals and the activated adsorption, and each one separately. Considering only the one pressure used throughout the rate measurements, 350 mm. Hg, curve 1 is taken from the isotherms in figure 3, and shows the total amount adsorbed at equilibrium at this pressure and at each of the temperatures considered. These amounts diminish regularly with increasing temperature except in the neighborhood of 150°C., where a sharp maximum is observed. It would be expected that this maximum, coming at such a high temperature, would be due to the activated adsorption rather than to the van der Waals variety.

Curve 3, which shows the 1-minute readings from the constant pressure

runs, bears out this expectation. This curve may be taken as representing the van der Waals adsorption alone at each of the temperatures. Evidently this type of adsorption falls off rapidly with rising temperatures, and exhibits no maxima or minima.

The difference between curves 1 and 3, then, must obviously represent the total *amount* of activated adsorption which takes place. This is represented graphically in curve 4, and the maximum in the region of 150°C. is very pronounced. The temperature range in which the catalytic efficiency of the chromite in assisting the combination of carbon monoxide and oxygen rises from about 40 per cent to 100 per cent is shown by the shaded area. In this range of temperature the amount of activated adsorption is considerably less than the amount of van der Waals adsorption, although it appears likely that this condition will be reversed at a somewhat higher temperature.

Curve 2 is the representation of the 30-minute readings taken from the curves of figure 1. The difference, then, between this curve and curve 3 will be the amount adsorbed at each temperature in the interval from one to thirty minutes, and will be proportional to the *rate* of the activated adsorption. This difference is represented by curve 5. It is evident that there is a maximum in the rate of the activated adsorption at about the same temperature at which we find the maximum in the extent to which it takes place.

These maxima in the amount of activated adsorption and in its rate suggest that perhaps there are two distinctly separate and entirely different processes taking place at the surface in addition to the van der Waals adsorption, which, for the moment, we are neglecting. Both of these processes, of course, would be included in a general definition of adsorption as any way in which a gas is taken up by a solid. But although each takes place at a measurable rate, the amount of one falls off with rising temperatures, whereas on the contrary, the amount of the other becomes greater as the temperature becomes higher.

In figure 5a the solid line curve is a duplicate of curve 4 in figure 4. Similarly, in figure 5b the solid curve is a duplicate of curve 5 in figure 4. In each case the broken-line curves marked a and b are arbitrarily drawn, regular curves which, when added together, give the curves with the maxima.

It does not seem wholly improbable that what we have been considering, then, as the activated adsorption of carbon monoxide on the chromite surface might possibly be really the summation of two distinctly separate processes, which, although in no sense do they work at cross purposes, nevertheless vary in a different way with temperature. These two processes, if such exist, could then be represented by curves of the type of those drawn in broken lines in figures 5a and 5b.

In figure 5a these curves will represent the extent to which these processes take place before equilibrium is reached at a pressure of 350 mm. Hg and the temperatures indicated, while the curves of figure 5b would be proportional to the rates at which the processes take place.

If we may represent the adsorption as the sum of two such hypothetical processes, one of them, that represented by b, diminishes with rising temperature, not only as regards the extent to which it occurs, but also in the rate at which it takes place.

It must be remembered that the differences between the adsorption curves for carbon monoxide are not large in comparison with the values involved. It may be possible that experimental errors are responsible for the maxima obtained in figures 4 and 5. However, the fact that the

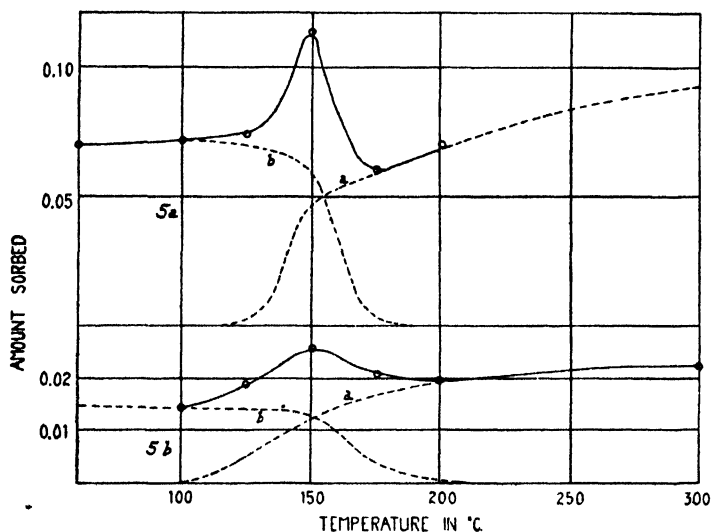


FIG. 5. Activated adsorption of carbon monoxide

maxima occur in the same temperature interval in each case and are so similar appears to bring the hypothetical processes suggested into the realm of possibility. If they do exist, perhaps one of the processes is one of solution, or diffusion, or some such phenomenon. At any rate, the exact nature of the two processes is of no importance as regards the relation of the adsorption process to catalytic activity, as we shall see directly.

In the range over which the efficiency of the chromite as a catalyst for the oxidation of carbon monoxide nears 100 per cent, the adsorption of carbon monoxide is falling off rapidly from its maximum, which makes it seem doubtful that it is of major importance in the mechanism of the catalytic reaction.

As the temperature is increased over this range, however, the adsorption

of oxygen rises extremely rapidly. It seems more likely, then, that the determining factor in the activity of the surface is the adsorption of oxygen. A suggested mechanism which seems reasonable is that the oxygen is first adsorbed on the chromite surface with an energy of activation of the order of those calculated. If the temperature is high enough so that the adsorption of the oxygen reaches sufficient proportions, any carbon monoxide passing over the catalyst surface either reacts directly with the adsorbed oxygen, or else is first adsorbed and then reacts, after which the carbon dioxide produced is desorbed.

Lory suggested that the catalytic activity was due to alternate oxidation of the chromite surface by oxygen and its reduction by carbon monoxide. If the term "adsorption" is defined as including *all ways* in which a gas is taken up at a solid surface, without regard to the nature of the binding between the surface and the adsorbed gas, adsorption would of course include the oxidation of the surface chromium atoms by gaseous oxygen. So in the strictest sense there is no real difference between the suggested mechanism and that proposed by Lory.

However, since the oxidation of the chromite is probably a process involving the addition of oxygen to the *surface* chromium atoms only, it seems wise to speak of it as an adsorption process, thus emphasizing the fact that it is a surface phenomenon,—for the surface is all-important in contact catalysis. At least, until it may be shown that the binding of the adsorbed gas to the surface is identical with that between atoms of the surface material and of the gas in their known compounds, it appears more to the point to use the term "adsorption" rather than "oxidation" to describe the process.

REFERENCES

- (1) BENTON, A. F.: Trans. Faraday Soc. **28**, 202 (1932).
- (2) BURRAGE, L. J.: Trans. Faraday Soc. **28**, 192-4 (1932).
BURRAGE, L. J.: Trans. Faraday Soc. **29**, 677-8 (1933).
- (3) GARNER, W. E.: Trans. Faraday Soc. **28**, 261 (1932).
- (4) LOCKWOOD, W. H.: J. Phys. Chem. **38**, 735-46 (1934).
- (5) LORY, E. C.: J. Phys. Chem. **37**, 685-92 (1933).
- (6) MCKINNEY, PAUL: J. Phys. Chem. **37**, 381 (1933).
- (7) TAYLOR, H. S.: J. Am. Chem. Soc. **53**, 578-97 (1931).
- (8) TAYLOR, H. S., AND STROTHER, C. O.: J. Am. Chem. Soc. **56**, 586-91 (1934).

PENETRATION OF SOLAR AND COSMIC RAYS INTO FRESH WATER LAKES

GEORGE A. LINHART

Department of Chemistry, Riverside Junior College, Riverside, California

Received May 2, 1935

The purpose of the present article is to show that the equation given in a recent paper (2), expressing the relation between turbulence and depth of the ocean, applies equally well to the decrease in temperature and to

TABLE 1
Relation between temperature and depth

LAKE CAYUGA			LAKE SENECA		
$\theta_{\infty} = 16.0; K = 6.004; \log k = -7.90156$			$\theta_{\infty} = 16.0; K = 4.142; \log k = -5.31622$		
<i>D</i>	<i>t</i>	θ	<i>D</i>	<i>t</i>	θ
<i>meters</i>	$^{\circ}\text{C.}$		<i>meters</i>	$^{\circ}\text{C.}$	
0	20.0	0.0	0	20.0	0.0
10	19.8	0.2	5	19.4	0.6
14	19.6	0.4	10	19.0	1.0
15	19.0	1.0	12	18.8	1.2
16	18.5	1.5	15	18.4	1.6
17	16.1	3.9	16	17.3	2.7
18	13.8	6.2	17	14.9	5.1
19	11.5	8.5	18	12.3	7.7
20	10.1	9.9	19	11.1	8.9
25	7.9	12.1	20	10.2	9.8
30	5.9	14.1	25	6.8	13.2
40	4.8	15.2	30	5.8	14.2
50	4.5	15.5	40	4.8	15.2
60	4.5	15.5	50	4.3	15.7
70	4.4	15.6	70	4.2	15.8
80	4.2	15.8	80	4.2	15.8
100	4.1	15.9	100	4.1	15.9
121	4.1	15.9	120	4.1	15.9

the penetration of solar heat and cosmic rays with increase in depth of fresh water lakes. Of the accumulated data given in the literature (3), two examples of each topic will suffice to illustrate these phenomena.

The methods of calculation and of tabulation are fully discussed in the paper referred to (2). The results of the present calculations are presented in three tables and are illustrated graphically in six figures. In

TABLE 2
Relation between heat and depth

LAKE CATUGA			LAKE SENECA		
$H_{\infty} = 26900; K = 2.483; \log k = -2.83347$			$H_{\infty} = 32900; K = 1.850; \log k = -2.09663$		
<i>D</i>	<i>-H</i>	<i>H</i>	<i>D</i>	<i>-H</i>	<i>H</i>
<i>meters</i>	<i>calories</i>	<i>calories</i>	<i>meters</i>	<i>calories</i>	<i>calories</i>
0	26900	0	0	32900	0
10	18600	8300	10	21000	11900
20	6900	20000	20	10800	22100
30	3100	23800	30	6600	26300
40	1800	25100	40	4500	28400
50	1400	25500	50	3300	29600
60	1100	25800	60	2600	30300
70	860	26040	70	2000	30900
80	590	26310	80	800	32100
100	320	26580	100	800	32100
			150	290	32610

TABLE 3
Relation between depth and cosmic ray ionization

LAKE ARROWHEAD				GEM LAKE			
$I_{\infty} = 53.00; K = 1.043; \log k = -0.58787$				$I_{\infty} = 80.00; K = 1.113; \log k = -0.47993$			
<i>D</i>	<i>I' (obsd.)</i>	<i>I' (calcd.)</i>	<i>I</i>	<i>D</i>	<i>I' (obsd.)</i>	<i>I' (calcd.)</i>	<i>I</i>
<i>meters</i>				<i>meters</i>			
0.82	43.80	43.80	9.20	0.85	64.10	62.70	17.30
1.50	37.50	38.00	15.00	1.00	60.10	60.10	19.90
2.00	33.50	34.49	18.41	2.00	43.80	46.61	33.39
3.00	29.50	29.25	23.75	4.00	30.40	31.38	48.62
4.00	25.50	25.38	27.72	43.00	3.62	3.52	76.48
5.00	23.10	22.17	30.77	50.00	3.30	2.96	77.04
6.00	21.10	19.79	33.19	60.00	2.49	2.48	77.52
6.25	20.60	19.29	33.71	72.55	2.00	2.00	78.00
8.25	17.33	15.90	37.10				
10.64	14.52	13.10	39.90				
15.90	10.23	9.43	43.57				
21.10	7.89	7.37	45.63				
26.25	6.07	6.20	46.80				
30.35	5.21	5.26	47.74				
37.05	4.25	4.35	48.65				
42.78	3.79	3.76	49.24				

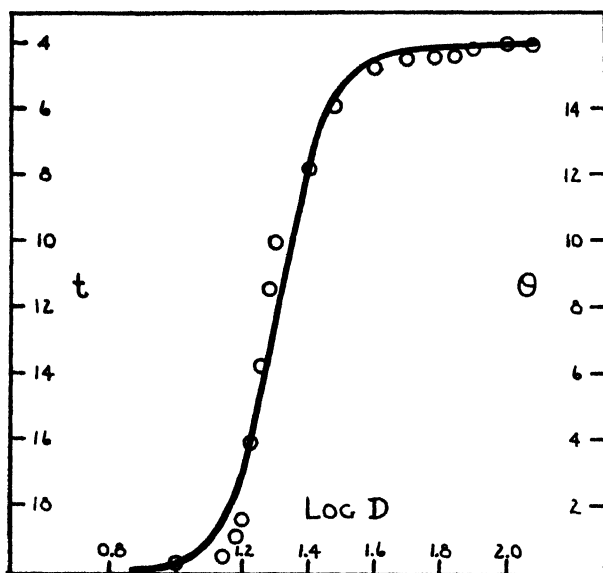


FIG. 1. Relation between temperature and depth—Lake Cayuga

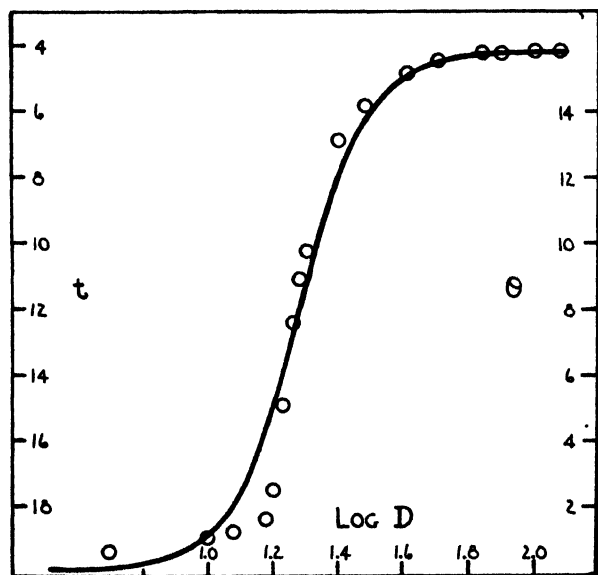


FIG. 2. Relation between temperature and depth—Lake Seneca

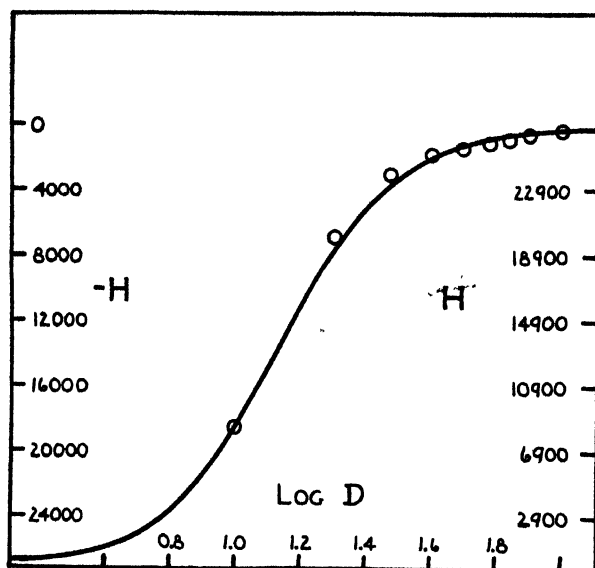


FIG. 3. Relation between heat and depth—Lake Cayuga

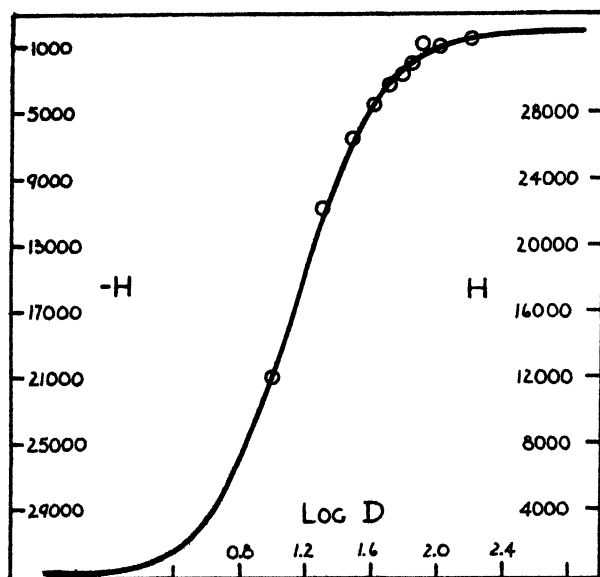


FIG. 4. Relation between heat and depth—Lake Seneca

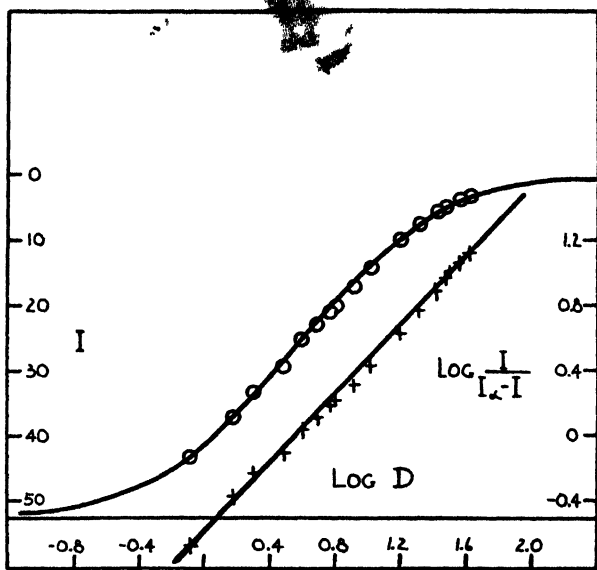


FIG. 5. Relation between depth and cosmic ray ionization—Lake Arrowhead

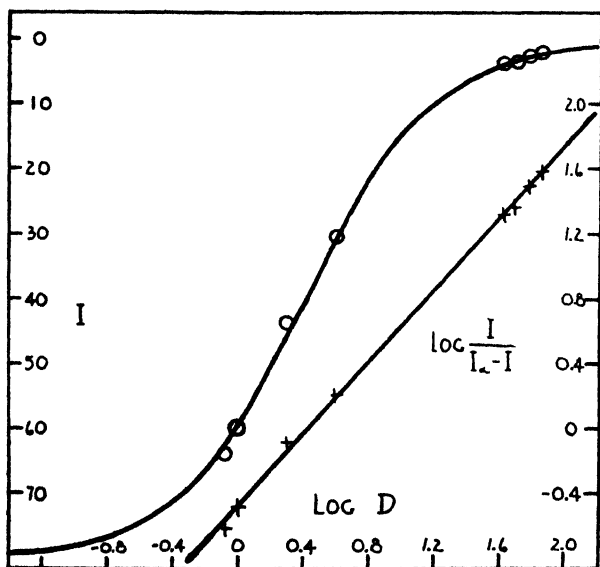


FIG. 6. Relation between depth and cosmic ray ionization—Gem Lake

table 1 are given the depths (D), the temperatures (t), and the total drop in temperature at each point (θ); in table 2, the depths (D), the solar heat ($-H$) in calories per unit of surface, and the total drop in heat at each point (H); and in table 3, the depths (D), the cosmic ray ionizations (I') per unit of surface per second, and the total drop in cosmic ray ionization at each point (I).

CONSTRUCTION OF THE GRAPHS

The constants (K and $\log k$) necessary for the construction of figures 1 and 2 were obtained from the data given in table 1 and the straight line equation

$$\log \theta / (\theta_{\infty} - \theta) = K \log D + \log k$$

those for the construction of figures 3 and 4, from the data given in table 2 and the equation

$$\log H / (H_{\infty} - H) = K \log D + \log k$$

and those for the construction of figures 5 and 6, from the data given in table 3 and the equation

$$\log I / (I_{\infty} - I) = K \log D + \log k$$

The quantities with the infinity subscripts (θ_{∞} , H_{∞} , and I_{∞}) were readily found from the graphs of the respective equations, which may be written in the general form

$$y = y_{\infty} k e^{K \log x} / (1 + k e^{K \log x})$$

This is obvious from the symmetry of the curve when y is plotted against $\log x$; for if the second derivative of y with respect to $\log x$ is placed equal to zero, $y = \frac{1}{2}y_{\infty}$. The values of these quantities, together with those for K and for $\log k$, are given at the head of each table.

DISCUSSION OF THE RESULTS

A glance at the graphs will show that the experimental values distribute themselves closely along the calculated curves, and, considering the uncontrollable experimental conditions, the fit in each case is as good as can be expected. This is especially true of the experimental points in figures 1, 2, 3, and 4. However, the experimental values shown in figures 5 and 6 represent a much higher degree of experimental control, and it seemed worthwhile, therefore, to place in table 3 calculated values alongside the experimental ones for comparison. The agreement is quite satisfactory.

In conclusion it may be noted that the similarity in the behavior of the three processes, presented in the three tables and in the six graphs, is not accidental. A comprehensive treatment of these and of similar processes, including the derivation of the general equation, is reserved for a final paper.

REFERENCES

- (1) BIRGE AND JUDAY: Alimnological Study of the Finger Lakes of New York State; Wisconsin Geographical and Natural History Survey, Madison, Wisconsin.
- (2) LINHART: The American Mathematical Monthly **XLII**, 224 (1935).
- (3) MILLIKAN AND CAMERON: Phys. Rev. **37**, 235 (1931).

CARBON DIOXIDE CLEAVAGE FROM DIBROMOMALONIC ACID. II

JYTTE MUUS

The University Institute of Biochemistry, Copenhagen, Denmark

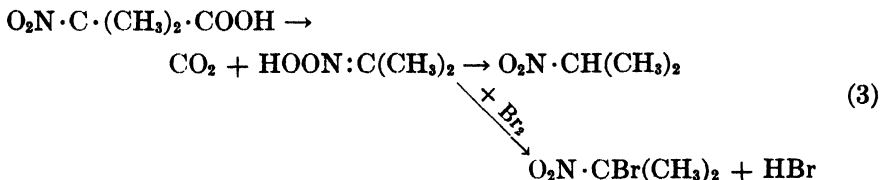
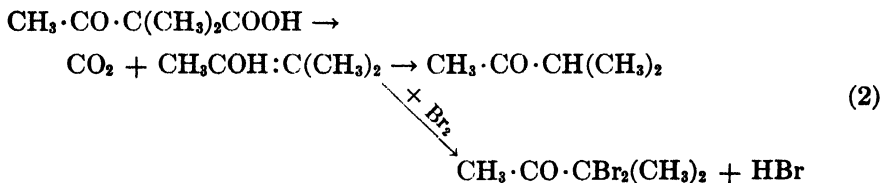
Received May 9, 1935

The decomposition of dibromomalonic acid into carbon dioxide and dibromoacetic acid

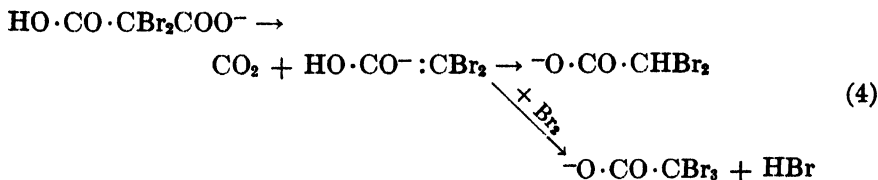


was studied in a previous paper (1). It was shown that the univalent ion decomposes spontaneously, the undissociated acid and the divalent ion being stable.

The carbon dioxide cleavage of β -keto- and α -nitro-carboxylic acids has been examined by Pedersen (2). From the fact that α,α -dimethylacetoacetic acid and α,α -dimethylnitroacetic acid take up bromine with the same velocity as they decompose, he concludes that an intermediate unsaturated compound is first formed by the cleavage:



The structure of dibromomalonic acid bears some analogy to that of β -keto acids. A mechanism analogous to that of scheme 2 is therefore suggested:



In order to test this suggestion some bromination experiments were carried out. It was shown that bromine is taken up during the decomposition. Since neither dibromoacetic acid nor dibromomalonic acid reacts with bromine under the experimental conditions, an intermediate product is surely responsible for the disappearance of bromine.

EXPERIMENTAL

In order to compare the results with those of the previous communication (1) the experiments were carried out at 25°C. and in the following solutions of hydrochloric acid and potassium chloride: x *M* HCl + $(1 - x)$ *M* KCl; x *M* HCl + $(0.2 - x)$ *M* KCl; and x *M* HCl + $(0.1 - x)$ *M* KCl.

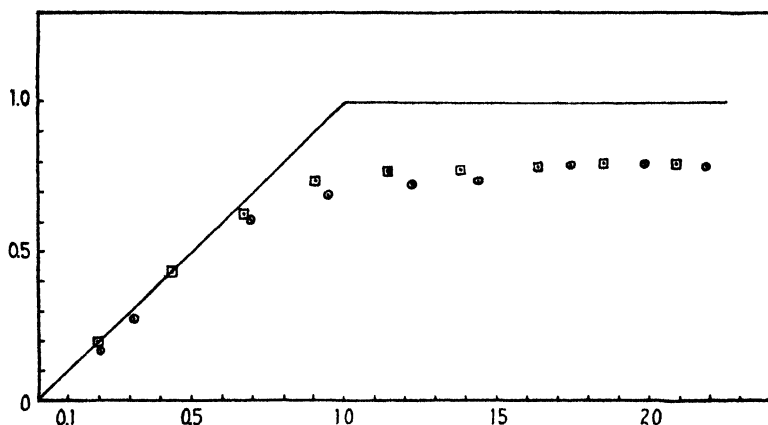
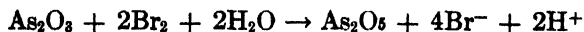


FIG. 1. Abscissa: moles of bromine added per mole of dibromomalonic acid. Ordinate: moles of bromine used per mole of dibromomalonic acid. $C_{Br_2C(COOH)_2} = 7.26 \times 10^{-3}$. — theoretical value if all the dibromomalonic acid reacts according to scheme 4b. □ □, experiments in 0.1 *N* hydrochloric acid; ○ ○, experiments in 0.1 *N* hydrochloric acid and 0.9 *N* potassium chloride.

In addition, known amounts of bromine and dibromomalonic acid were present. A suitable time after the start of the reaction an excess of 0.1 *N* arsenious acid was added. The arsenious acid reacts instantaneously with bromine.



but does not react with the other substances present. The excess of arsenious acid was titrated with bromine water.

In most experiments the dibromomalonic acid was about 0.007 *M*. The amount of bromine taken up during the reaction increases with increasing bromine concentration. However, when the initial concentration of bromine is about 0.012 *M*, further increase does not increase the amount of bromine taken up (figure 1).

The amount of bromine disappearing when the reaction is allowed to proceed until completion also depends upon the concentration of hydrochloric acid, as shown in table 1.

The fact that only a fraction of dibromomalononic acid reacts with bromine, and that this fraction is independent of the bromine concentration within a large range of concentration, is not in accordance with scheme 4. Part of the dibromomalononic acid must be converted into dibromoacetic acid without forming an intermediate product capable of reacting with bromine.

The following mechanism of reaction is suggested.

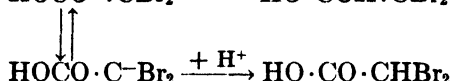
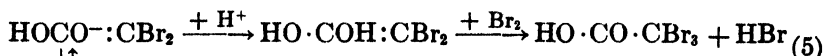
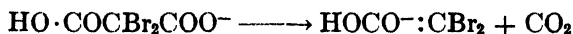


TABLE 1

Bromine taken up by dibromomalononic acid

$\text{CBr}_3\text{C}(\text{COOH})_2 = 7 \times 10^{-3}$; $\text{CBr}_2 = 12 \times 10^{-3}$. n = moles of bromine reacting per mole of dibromomalononic acid

HCl	$\frac{x \text{ M HCl}}{(1-x) \text{ M KCl}}$	$\frac{x \text{ M HCl}}{(0.2-x) \text{ M KCl}}$	$\frac{x \text{ M HCl}}{(0.1-x) \text{ M KCl}}$
	n	n	n
<i>M</i>			
1.00	0.852		
0.75	0.859		
0.50	0.868		
0.25	0.838		
0.20	0.815	0.820	
0.10	0.792	0.795	0.781
0.08	0.753	0.780	0.770
0.05	0.718		

It fulfills the requirement, and it seems likely that the first step of the reaction is much slower than the following and thus determines the rate of the reaction. But of course other mechanisms may be proposed.

Without stating anything definite about the mechanism of the reaction, it is obvious that two reactions take place simultaneously. The one leads directly to dibromoacetic acid, the other to the formation of a product which reacts with bromine. If the ratio of the velocities of these reactions is $(1-n):n$, we see that, at the time t , when c moles per liter of carbon dioxide have been split off, nc moles per liter of bromine have been used. If the initial concentration of dibromomalononic acid is c_0 , nc_0 moles per liter of bromine have been used at the end of the reaction. From the expression

$$-kt = \log \frac{c_0 - c}{c_0} = \log \frac{nc_0 - nc}{nc_0}$$

it is readily seen that k , computed by means of the development of carbon dioxide, should be identical with k computed from the disappearance of bromine, when we substitute the amount of bromine actually taken up for the amount which would be taken up if only tribromoacetic acid were formed.

In table 2 k_1 is the velocity constant previously found for the carbon dioxide cleavage. k_2 is the velocity constant of the bromination computed as just explained. k_2 does not differ much from k_1 , indicating that the assumption of the formation of an intermediate unsaturated compound is correct.

In order to show that the presence of bromine does not interfere with the first step of reaction 5, the velocity of the carbon dioxide cleavage was determined by the method previously used in 0.1 M hydrochloric acid,

TABLE 2
Velocity constants of the bromination
 $C_{Br_2C(COOH)_2} = 7 \times 10^{-3}$; $C_{Br_2} = 12 \times 10^{-3}$; $t = 25^\circ C$.

HCl	$\frac{x}{1-x} M$ HCl (1 - x) M KCl		$\frac{x}{0.2-x} M$ HCl (0.2 - x) M KCl		$\frac{x}{0.1-x} M$ HCl (0.1 - x) M KCl	
	$k_1 \times 10^3$	$k_2 \times 10^3$	$k_1 \times 10^3$	$k_2 \times 10^3$	$k_1 \times 10^3$	$k_2 \times 10^3$
<i>M</i>						
1.00	2.83	3.07				
0.75	3.25	3.51				
0.50	3.99	4.30				
0.25	4.41	4.71				
0.20	4.56	4.70	4.07	4.46		
0.10	4.48	4.75	4.26	4.50	4.31	4.64
0.08	4.22	4.87	4.40	4.46	4.25	4.68
0.05	4.10	5.64			4.24	4.73

containing bromine of the same concentration as in the bromination experiments. Without bromine the velocity constant was 4.31×10^{-3} , with bromine 4.30×10^{-3} .

SUMMARY

The mechanism of the decomposition of dibromomalonic acid has been studied.

It has been found that simultaneously with the carbon dioxide cleavage bromine was taken up. The rate of the reaction of the bromination was approximately the same as that of the carbon dioxide cleavage.

From this result it was concluded that the first step of the reaction was the formation of an unsaturated compound.

REFERENCES

- (1) MUUS, JYTTE: *J. Phys. Chem.* **39**, 343 (1935).
- (2) PEDERSEN, K. J.: *J. Phys. Chem.* **38**, 559 (1934).

MOLECULAR DIMENSIONS FROM VISCOSITY STUDIES¹

ROBERT M. THEIS² AND HENRY B. BULL

*Division of Agricultural Biochemistry, University of Minnesota, Minneapolis,
Minnesota*

Received June 20, 1935

THEORETICAL CONSIDERATIONS

The viscosity of a bulk liquid is known to be increased by the presence of a suspended particle. The complete mathematical treatment of this problem for the case of spherical particles has been solved by Einstein (1).

Jeffery (5) has extended the work carried out by Einstein, for the case of ellipsoidal particles. Great difficulties were encountered in the solution of the problem and the results were left in a rather indeterminate form, owing to the fact that a number of motions were possible for a given set of boundary conditions.

Eisenschitz (2), assuming that the ellipsoidal particle so orients itself at the time $t = 0$ (beginning orientation) that its axes coincide with the principal axes of deformation of the fluid, calculated, both for pure motion of deformation and for plane laminar flow, the value of this numerical factor in terms of ratio of length to diameter. His results for plane laminar flow are as follows:

$$\frac{\eta}{\eta_0} = 1 + \frac{1.15 \frac{a}{b}}{\pi \log_e 2 \frac{a}{b}} \cdot \frac{v}{V}$$

where a = the long axis of the ellipsoid,

b = the short axis of the ellipsoid,

η and η_0 = viscosities of solution and solvent, respectively,

v = volume of particle, and

V = volume of solution.

We applied this equation to stearic acid dissolved in carbon tetrachloride as well as to lecithin in the same solvent.

¹ Published as Journal Series No. 1363, Minnesota Agricultural Experiment Station.

² This paper is taken from a thesis presented by Robert M. Theis to the Faculty of the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Master of Science, June, 1935.

VISCOSITY MEASUREMENTS

Measurements were made with the Ostwald type of viscosimeter. For 8 cc. of carbon tetrachloride the time of out-flow was about 90 seconds, while for the same volume of water it was over 120 seconds. The neck of the instrument was drawn out to about half its thickness to facilitate the recording of an accurate starting point. This narrow constriction was etched with hydrogen fluoride, as also was the capillary tube. The instrument was kept filled with cleaning solution when not in use, especially overnight. The densities of the solutions were determined by means of a pycnometer, which was accurately calibrated. As the apparatus must be extremely clean to get reliable measurements, the following procedure was followed: The apparatus was washed twice with waste carbon tetrachloride, once with pure carbon tetrachloride and once with acetone, and dried by evacuating.

The stearic acid used was recrystallized from benzene. It melted at 69°C., which indicated that it was quite pure. The solutions were prepared by dissolving a known weight of stearic acid in carbon tetrachloride and making up to correct volume. The data are given in table 1 and graphed in figure 1.

Fikentscher and Mark (3), taking into account the process of solvation, have proposed the following formula:

$$\frac{\eta}{\eta_0} - 1 = \frac{''a'' \Phi c}{100 - \Phi c}$$

where Φ is the volume occupied by 1 g. of substance in solution (volume of solvated particle), c the concentration in grams per 100 cc. of solution, and $''a''$ equals 2.5.

Φc in the denominator of the above expression is analogous to the b term in van der Waals' equation of gases. The value of the constant $''a''$ will be 2.5 for spherical particles only.

Treating $''a''$ and Φ as general constants and rearranging the above expression in the following form, one obtains:

$$\frac{c}{\eta_{sp}} = \frac{100}{a\Phi} - \frac{1}{a} c$$

where

$$\eta_{sp} = \frac{\eta}{\eta_0} - 1$$

The variables in this equation are $\frac{c}{\eta_{sp}}$ and c . If one plots $\frac{c}{\eta_{sp}}$ as ordinate and c as abscissa, as is done in figure 1, a straight line with intercept equal

to $\frac{100}{a\Phi}$ and with a negative slope of $1/a$ is obtained. From the values of the slope of the line and the ordinate intercept, a is 0.885 and Φ is 4.185 cc. per gram.

TABLE 1
Viscosity of solutions of stearic acid in carbon tetrachloride

CONCENTRATION IN GRAMS PER 100 CC. OF SOLUTION	η_r	c/η_{sp}
2.0	1.0809	24.72
1.5	1.059	25.33
1.0	1.0387	25.82
0.5	1.0186	26.87

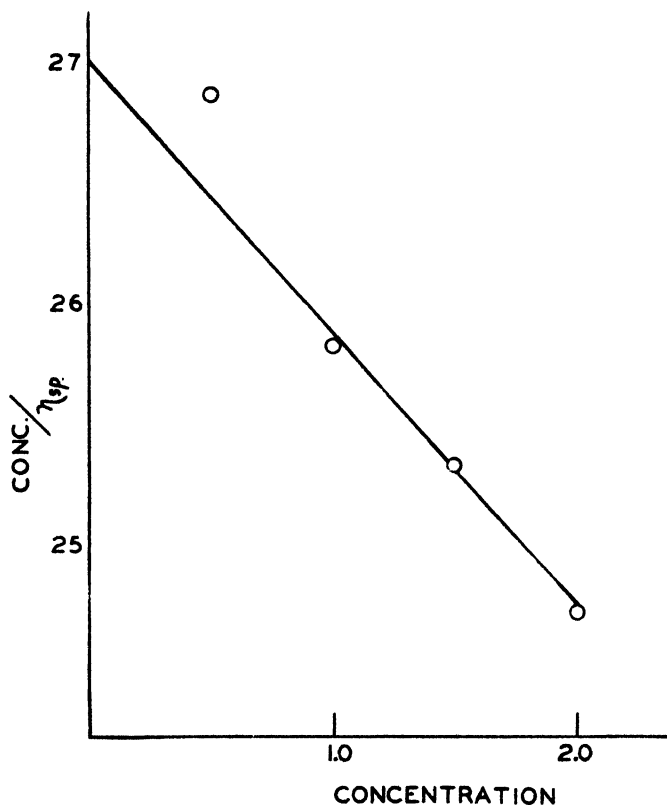


FIG. 1

The specific gravity of stearic acid at room temperature is approximately 0.85. This corresponds to a specific volume of 1.17 cc. On the other hand, the apparent specific volume from viscosity measurements turned out to

be 4.185, about 3.5 times the expected value. There is no reason to believe that a gram of substance should occupy the same volume in both the solid state and in solution. However, when solvation takes place, in the case of stearic acid, the carbon tetrachloride becomes part of the stearic acid particle, so that the apparent specific volume now becomes the volume occupied by 1 g. of stearic acid plus an unknown number of grams of carbon tetrachloride, but this total volume is calculated on the basis of 1 g. of stearic acid.

We do not know whether the solvent is included between the particles of solute or a shell of solvent is built around each particle. In either case the particle assumes a definite shape with some deformability, so that the solution still behaves as a homogeneous liquid. The value of the constant " a " (found) indicated that stearic acid does not form spherical particles in solution. Assuming that we are dealing with ellipsoids of revolution instead of spheres, we applied Eisenschitz's equation to determine what ratio of length to diameter corresponds to the value of the constant " a ," obtained experimentally. If we assume that the motion of the particle is plane laminar flow and that the ratio of length to diameter is 6 to 1, then the value of " a " by the above equation is:

$$a = \frac{0.159 (6/1)}{\log_{10} 12} = 0.884$$

which corresponds to the value of " a " (0.885), found experimentally.

From x-ray data of Francis, Piper, and Malkin (4) the diameter of a stearic acid molecule is 3.7 to 4.0 A.U. and the length of a single molecule is 23.4 A.U. (this is calculated on the basis of the above work). This will give us a ratio of length to diameter of approximately 6 to 1.

The lecithin was prepared by a modification of the method of Sueyoshi (7). The reagents were carefully purified and tested for their purity. Analysis of the lecithin gave the following results: total nitrogen, 1.835 weight per cent; phosphorus, 4.094 weight per cent; N:P ratio, 1:1.007; amino nitrogen, 0.39 weight per cent.

Van Slyke analysis shows a high contamination of cephalin (21 per cent), but since the N:P ratio is practically 1, it indicates that the material obtained is free from other lipids. The presence of cephalin would hardly affect viscosity measurements, as there is little difference between the molecular structure of lecithin and of cephalin.

In table 2 are the results of our viscosity measurements of lecithin in carbon tetrachloride at various concentrations. These values are graphed in figure 2.

Treating the data obtained for lecithin in the same way that we did for stearic acid, we found a similar relation between viscosity and concentration. A comparison of figures 1 and 2 will disclose the fact that the points

TABLE 2

Viscosity of solutions of lecithin in carbon tetrachloride

CONCENTRATION IN GRAMS PER 100 CC. OF SOLUTION	η_r	c/η_{sp}
11	1.4920	22.357
8	1.3318	24.111
5.7	1.2269	25.121
3.7	1.1410	26.24
1.8	1.0648	27.77
0.9	1.0259	34.74

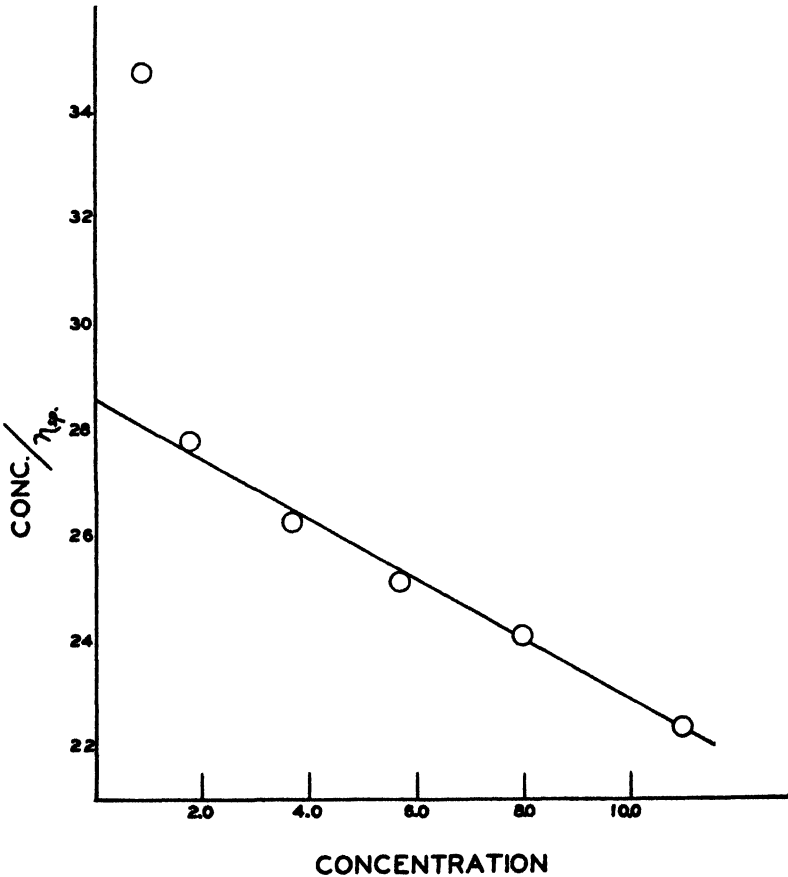


FIG. 2

do not lie on a straight line for small concentrations. If one rewrites the ordinate in the form $\frac{c\eta_0}{\eta - \eta_0}$ it can be seen that small errors in $\eta - \eta_0$ will greatly affect the results. This usually occurs for small concentrations where η is not much different from η_0 .

Carrying out the same sort of calculation for lecithin as for stearic acid, we found $\Phi = 1.99$ cc. per gram and $a = 1.76$.

Assuming that lecithin forms ellipsoidal particles and applying Eizenschitz's equation, " a " from experiment corresponds to a 17 to 1 ratio of length to diameter, i.e., if a/b is 17/1 then:

$$a = \frac{0.159(17)}{\log_{10} 34} = 1.76$$

According to Leathes (6) the cross section of a lecithin molecule is about 70 (A.U.),² which corresponds to a diameter of a little over 8 A.U. For a 17 to 1 ratio of length to diameter the length of lecithin molecules would have to be about 136 A.U. This corresponds to the length of four lecithin molecules in a straight chain.

CONCLUSIONS

The information which we hope to gain by this type of research is not as complete as expected. The discrepancy lies not in the fact that the measurements yield results which are not reliable, or that we are dealing with too complicated a material, but that we are handicapped in the application of equations based on purely theoretical grounds. Thus it can readily be seen that when one tries to apply the Eizenschitz equation to experimental results certain limitations arise, as for example: (1) The equation of Eizenschitz has been derived under the assumption that $a \gg b$. As the ellipsoidal particle approaches that of a sphere, the equation can no longer be applied. (2) The question arises as to whether the equation can be applied to cases where there is a formation of long chains.

If the ratio of length to diameter of lecithin is too small to apply the above equation to the results obtained, then lecithin must be approaching the form of an oblate or prolate spheroid. However, if we assume that the equation is applicable, then lecithin forms chains of four molecules on the average.

More experiments must be performed to determine the limitations of Eizenschitz equation, as well as the applicability of the same to associated systems.

SUMMARY

1. Viscosity measurements of stearic acid and lecithin dissolved in carbon tetrachloride were made at various concentrations, and a linear relation found when c/η_{sp} is plotted against c .

2. The application of the Eisenschitz equation to experimental results is discussed with reference to ratio of length to diameter of both stearic acid and lecithin.

REFERENCES

- (1) EINSTEIN: Ann. Physik **19**, 289-306 (1906); **34**, 591-2 (1911).
- (2) EISENSCHITZ: Z. physik. Chem. **158A**, 78-90 (1932).
- (3) FIKENTSCHER AND MARK: Kolloid-Z. **49**, 135-48 (1929).
- (4) FRANCIS, PIPER, AND MALKIN: Proc. Roy. Soc. London **128A**, 214-52 (1930).
- (5) JEFFERY: Proc. Roy. Soc. London **102A**, 161-79 (1922).
- (6) LEATHES: Lancet **206**, 853-6 (1925).
- (7) SUEYOSHI: J. Biochem. Japan **13**, 145-54 (1931).

THE PRODUCTION OF FURFURAL FROM XYLOSE SOLUTIONS BY MEANS OF HYDROCHLORIC ACID-SODIUM CHLORIDE SYSTEMS

ELLIS I. FULMER, L. M. CHRISTENSEN, R. M. HIXON, AND R. L. FOSTER

Department of Chemistry, Iowa State College, Ames, Iowa

Received May 23, 1935

I. INTRODUCTION

One of the outstanding achievements in the utilization of agricultural wastes in the manufacture of industrial chemicals is the development of the furfural industry. The furfural is produced by heating oat hulls at about 60 pounds pressure with about 5 per cent sulfuric acid for five or more hours (14, 16, 5). The yield is about 50 to 60 per cent of the theoretical. The studies reported in the present communication have to do with the production of furfural from strong xylose solutions by various combinations of hydrochloric acid and sodium chloride, in order to establish general principles of procedure which could be applied directly to the agricultural material or to the xylose-containing hydrolysates made therefrom. The presence of the salt decreases the solubility of the furfural, ensuring its more rapid and complete removal by the solvent. The salt likewise increases the activity of the acid. This latter phenomenon has been studied with reference to various hydrolytic actions (2, 3, 4, 6, 7, 8, 9, 10, 11, 20). In general, the hydrolytic action of a strong acid, such as hydrochloric acid, is proportional to the "apparent" hydrogen-ion concentration, which is conveniently expressed in terms of pH. So far as the authors are aware, this principle has not been applied to a dehydration action such as the production of furfural from xylose. Adams and Vorhees (1), Hurd and Isenhour (13, 14), and others have employed salts in this reaction for the purpose of reducing the solubility of the furfural in order to facilitate distillation.

II. GENERAL PROCEDURE AND PRELIMINARY EXPERIMENTS

A. General procedure

The aqueous xylose solutions plus the dehydrating agents were refluxed with an immiscible solvent in which furfural is very soluble. These solvents included benzene, toluene, and carbon tetrachloride. Toluene is the solvent employed in the studies here reported in detail. The purpose

of the solvent is twofold. It removes the furfural as formed, thus cutting down the opportunity for polymerization of the furfural in the presence of the dehydrating reagents, and it also permits the building up of high concentrations of furfural in the solvent, thus allowing an easy and economical separation by distillation.

The concentration of furfural in the toluene was determined by specific gravity measurement with a Westphal chainomatic balance. Quantitative experiments showed the specific gravity of toluene-furfural systems to be a linear function of the concentration of furfural. Toluene was refluxed with equal volumes of the sodium chloride-hydrochloric acid solutions of the strength employed in subsequent experiments; there was no significant change in specific gravity. The toluene solutions of furfural, obtained by action of the sodium chloride-hydrochloric acid systems upon xylose, were shaken with sodium sulfite. The specific gravity was restored to that of the pure toluene. These toluene-furfural systems were subjected to fractional distillation. The distillation curve corresponded to that obtained for known furfural-toluene systems. The furfural so obtained was identical with pure furfural.

The xylose was analyzed by three different methods, those of Shaffer and Hartmann (18), Slater and Acree (19), and Kline and Acree (15). The purity was found to be 95.5, 96.2, and 95.5 per cent by the respective procedures, with an average value of 95.7 per cent. Since the theoretical yield of furfural from pure xylose is 64 per cent, the maximum yield from the xylose used would be about 61 per cent.

B. The influence of volume ratios upon yields of furfural

In table 1 are given data showing the influence of volume ratios upon the yield of furfural from 20 per cent xylose refluxed for five hours in the presence of 0.50 *N* hydrochloric acid-40 per cent sodium chloride. The concentrations of sodium chloride and of xylose throughout this paper are expressed in grams per 100 cc. of acid used. It is evident that the yield of furfural increased slightly up to a ratio of 67:100 and was practically constant beyond that point. In subsequent experiments the toluene and aqueous systems were employed in equal volumes.

C. Influence of xylose concentrations on yields of furfural

In table 2 are given data on the yield of furfural from various concentrations of xylose refluxed for five hours in the presence of 0.50 *N* hydrochloric acid-40 per cent sodium chloride. The results show a decrease in yield with increase in xylose concentration. In subsequent work a xylose concentration of 20 per cent was employed.

D. The effect of certain salts

Preliminary experiments showed some interesting effects of salts upon strong xylose solutions. For example, 250 cc. of water was added to 75 g.

of xylose and 75 g. of ammonium chloride. The solution was heated on a hot plate; a strong odor of furfural was soon evident. However, the furfural could not be readily extracted from the mixture by means of benzene, toluene, or carbon tetrachloride. On vigorous shaking, the mixture proved to be an excellent emulsifying agent for the solvent. When subjected to distillation the furfural began to distill over at about 110°C. At 120°C. the mixture had a strong tendency to foam and the furfural distilled in such amounts that each drop was diphasic. These results indicate the

TABLE 1

Effect of varying volume ratios of toluene with 20 per cent xylose solution with 0.50 N hydrochloric acid and 40 per cent sodium chloride for five hours

TOLUENE	AQUEOUS SOLUTION	TOLUENE PER 100 CC. OF AQUEOUS SOLUTION	YIELD OF FURFURAL PER 100 G. OF XYLOSE
cc.	cc.	cc.	grams
20	103	19.4	29.8
35	93	37.6	30.7
50	93	53.8	30.7
100	159	62.9	31.8
80	119	67.2	33.3
125	184	67.9	33.2
65	93	69.9	34.0
150	188	80.0	34.0
50	50	100.0	33.6

TABLE 2

Effect of varying concentrations of xylose, using 0.50 N hydrochloric acid and 40 per cent sodium chloride for five hours

XYLOSE	YIELD OF FURFURAL PER 100 G. OF XYLOSE	PER CENT OF THEORETICAL YIELD	XYLOSE	YIELD OF FURFURAL PER 100 G. OF XYLOSE	PER CENT OF THEORETICAL YIELD
per cent			per cent		
4	42.5	70	30	29.4	48
8	40.0	66	40	28.0	46
10	39.4	65	50	25.5	42
15	36.0	59	60	22.7	37
20	33.6	55			

formation of an intermediate product, which is insoluble in the solvents employed but which at higher temperatures yields furfural readily. Similar results were obtained with ammonium sulfate, ammonium dihydrogen phosphate, and ammonium tartrate.

Strong solutions of aluminum sulfate and of zinc chloride also gave furfural on boiling with concentrated solutions of xylose, but in these instances the furfural was readily extracted with the solvents. Strong solutions of sodium chloride, calcium chloride, or of sodium sulfate did not lead to the formation of furfural.

TABLE 3

Yields of furfural from 20 per cent xylose solution with various combinations of hydrochloric acid-sodium chloride

NORMALITY OF HCl	NaCl	pH	2 HOURS			4 HOURS			6 HOURS			8 HOURS		
			<i>f</i>	<i>f</i> ₁	<i>f</i> ₂	<i>f</i>	<i>f</i> ₁	<i>f</i> ₂	<i>f</i>	<i>f</i> ₁	<i>f</i> ₂	<i>f</i>	<i>f</i> ₁	<i>f</i> ₂
<i>N</i>	<i>per cent</i>													
0.25	0	0.60	0	1.1	1.1	2.8	2.2	2.2	1.8	2.7	2.7	4.7	3.7	3.7
	5	0.46	1.1	1.5	1.5	3.1	3.1	3.1	2.5	3.7	3.7	5.1	5.0	5.0
	10	0.32	1.7	2.0	2.0	4.0	4.2	4.2	4.3	5.0	5.0	6.3	6.8	6.8
	15	0.18	2.5	2.8	2.8	6.0	5.7	5.5	7.2	7.1	6.8	9.4	9.3	8.7
	20	0.04	3.7	3.8	3.8	7.9	7.9	7.4	8.1	9.5	8.9	13.0	12.6	11.5
	25	-0.10	5.1	5.1	5.1	10.5	10.5	10.0	12.6	12.9	12.3	17.3	17.4	15.1
	30	-0.24	7.4	7.1	7.1	13.6		13.2	16.3		16.6	20.1		20.0
	35	-0.38	10.2	10.0	10.0	16.8		17.8	19.6		22.4	24.6		25.7
	40	-0.52	12.4		12.6	19.3		22.9	23.8		26.3	26.4		30.2
	45	-0.66				20.6		26.9	26.4		30.9	30.4		33.1
0.50	0	0.27	1.6	2.2	2.3	5.2	4.5	4.6	3.4	5.9	5.5	8.3	6.5	7.1
	5	0.13	3.9	3.1	3.2	7.1	6.2	6.2	7.3	7.9	7.6	8.7	8.9	9.5
	10	-0.01	4.3	4.3	4.3	8.8	8.5	8.5	11.7	11.2	10.5	13.2	12.3	12.9
	15	-0.15	6.0	5.8	5.8	12.2	11.5	11.0	15.5	13.5	13.5	18.2	16.6	16.6
	20	-0.29	8.4	7.9	7.9	15.9	15.5	15.1	19.8	20.4	18.2	22.8	22.9	22.4
	25	-0.43	10.7	10.7	10.7	19.3	20.9	19.5	24.8		24.0	28.8		28.8
	30	-0.57	14.8	14.8	14.8	23.2		23.4	28.8		28.8	32.9		32.4
	35	-0.71	17.2		19.0	27.5		28.2	32.7		32.4	33.4		33.9
	40	-0.85	19.3		22.4	30.4		30.9	36.1		36.3	34.0		35.5
	45	-0.99	19.3		25.1	30.4		32.4	33.5		37.1	36.9		38.0
0.75	0	0.07	3.7	3.7	3.6	5.6	6.6	6.9	5.0	8.5	8.5	11.5	10.7	10.7
	5	-0.07	5.3	5.1	4.9	9.7	9.1	9.1	12.8	11.8	11.2	15.3	14.8	14.5
	10	-0.21	6.9	7.1	6.6	13.0	12.6	12.6	16.7	16.7	15.1	22.4	20.4	18.6
	15	-0.35	9.6	9.5	9.1	18.3	18.2	17.0	21.8	21.9	20.9	26.4	26.3	24.5
	20	-0.49	13.2	13.2	12.6	22.5	23.4	21.4	25.7		25.7	32.4		31.6
	25	-0.63	18.0	18.2	17.8	26.8		26.9	31.8		30.9	35.8		33.1
	30	-0.77	20.2		21.4	31.6		30.2	33.6		33.9	37.6		34.7
	35	-0.91	24.4		24.5	34.4		33.1	39.0		36.3	39.8		36.3
	40	-1.05	24.6		27.5	34.7		34.7	39.0		38.0	40.4		38.0
	45	-1.19	25.7		29.5	35.6		35.5	40.8		40.7	40.3		39.8
1.00	0	-0.01	2.5	4.2	4.2	9.4	8.9	6.8	10.2	10.0	10.5			
	5	-0.15	5.0	5.6	5.7	12.7	12.0	11.0	16.4	15.5	14.5			
	10	-0.29	7.7	7.8	7.8	17.5	16.6	15.1	20.3	20.9	19.1			
	15	-0.43	10.7	10.7	10.5	21.2	22.4	20.4	25.8		24.5			
	20	-0.57	15.3	14.4	14.5	25.9		25.7	32.0		28.8			
	25	-0.71	19.3	19.5	17.4	31.5		29.5	34.0		33.1			
	30	-0.85	23.0		22.9	34.2		31.6	35.2		33.8			
	35	-0.99	25.5		26.3	34.8		34.7	36.8		34.5			
	40	-1.13	26.8		28.8	38.1		35.5	37.5		35.5			
	45	-1.27	26.2		30.9	37.8		36.3	38.4		36.3			

TABLE 3—*Concluded*

NORMALITY OF HCl	NaCl	pH	2 HOURS			4 HOURS			6 HOURS			8 HOURS		
			<i>f</i>	<i>f</i> ₁	<i>f</i> ₂	<i>f</i>	<i>f</i> ₁	<i>f</i> ₂	<i>f</i>	<i>f</i> ₁	<i>f</i> ₂	<i>f</i>	<i>f</i> ₁	<i>f</i> ₂
<i>N</i>	<i>per cent</i>													
1.50	0	-0 24	4 1	7.2	7 1	13 9	13 5	13 5	19 8	19 1	20 0			
	5	-0 38	9 7	9 8	9 5	18 9	18 6	18 6	25 4	25 7	25 7			
	10	-0 52	14 5	13 5	13 2	24 0	25 1	23 4	30 3		31 6			
	15	-0 66	18 0	18 2	18 2	29 0		28 2	34 4		33 8			
	20	-0 80	22 9		22 4	33 0		30 9	36 0		34 7			
	25	-0 94	26 2		25 1	35 7		33 9	35 1		35 0			
	30	-1 08	31 0		28 8	36 9		35 5	34 0		35 0			
	35	-1 22	31 6		36 8	36 8		36 3	34 2		35 0			
	40	-1 36	32 8		31 6	39 2		36 7	34 9		35 0			
	45	-1 50				38 9		37 1	34 7		35 0			
2.00	0	-0 45	13 4	12 6	11 5	17 4	17 0	20 4						
	5	-0 59	17 6	17 4	15 9	23 4	23 4	24 6						
	10	-0 73	23 5	23 4	21 9	28 6		28 8						
	15	-0 87	28 3		24 6	32 4		31 6						
	20	-1 04	31 5		28 2	33 8		33 9						
	25	-1 18	35 5		30 9	34 0		35 5						
	30	-1 32	36 0		32 4	35 0		35 9						
	35	-1 46	36 4		33 9	34 7		36 3						
	40	-1 60	35 9		35 5	36 0		36 3						
	45	-1 74	36 7		36 0	36 4		36 7						

f = experimental yield of furfural, in grams produced per 100 grams of xylose.

*f*₁ = yield calculated by the relation $\log f = a + 0.028 \times \text{per cent NaCl}$.

*f*₂ = yield as read from a diagram of $\log f$ against pH for all values for all combinations of sodium chloride and hydrochloric acid.

III. THE YIELD OF FURFURAL IN THE PRESENCE OF VARIOUS COMBINATIONS OF SODIUM CHLORIDE-HYDROCHLORIC ACID

In table 3 are given data for the yields of furfural from 20 per cent xylose in the presence of 0.25, 0.50, 0.75, 1.00, 1.50, and 2.00 *N* hydrochloric acid with concentrations of sodium chloride from 0 to 45 per cent for various periods of time. The data show the marked effect of the presence of the salt. The highest yield without salt is 20 per cent at 1.50 *N* hydrochloric acid after six hours. This same yield was given in two hours by approximately the following hydrochloric acid-sodium chloride systems: 0.50 *N*-40 per cent; 0.75 *N*-30 per cent; 1.00 *N*-25 per cent; and 1.50 *N*-15 per cent. The highest yields are 35 to 40 per cent, or 57 to 65 per cent of theoretical.

IV. THE RELATION OF YIELD OF FURFURAL TO THE pH OF THE SODIUM CHLORIDE-HYDROCHLORIC ACID SYSTEMS

In table 4 are given data for the pH values of 0.25 *N* hydrochloric acid in the presence of varying concentrations of sodium chloride. These values

were determined potentiometrically. No corrections were made for diffusion potential. Data are also presented showing the effect of the sodium chloride upon the solubility of the furfural. While the "apparent" hydrogen-ion concentration increased nearly ninefold, the solubility is decreased only to one-third.

The relation between pH and concentration of sodium chloride for table 4 is

$$\text{pH} = 0.60 - 0.028 \times \text{per cent NaCl} \quad (1)$$

Also, for a given time period, the yield of furfural is a linear function of the "apparent" hydrogen-ion concentration, through a major portion of the curve. The deviation from this linear relationship is associated with

TABLE 4

Effect of sodium chloride upon the pH of 0.25 N hydrochloric acid and upon the solubility of furfural at 25°C.*

PER CENT NaCl	pH	"APPARENT" CH^+	RELATIVE CH^+	FURFURAL IN TOLUENE	FURFURAL IN WATER	DISTRIBUTION RATIO
0	0.57	0.273	1.00	2.90	0.60	0.207
5	0.46	0.346	1.27	2.98	0.52	0.174
10	0.32	0.476	1.74	3.06	0.44	0.144
15	0.18	0.654	2.39	3.10	0.40	0.129
20	0.07	0.860	3.15	3.14	0.36	0.114
25	-0.09	1.228	4.50	3.19	0.31	0.097
30	-0.25	1.763	6.46	3.20	0.29	0.091
35	-0.37	2.331	8.54	3.25	0.25	0.077

* Seven per cent furfural in toluene used, 50 cc. of 0.25 N hydrochloric acid, and 50 cc. of toluene-furfural solution.

decreased yield, due to polymerization of the furfural and other factors which cause a marked darkening of the reaction mixture. During the range for which equation 1 holds,

$$\log f = a + 0.028 \times \text{per cent NaCl} \quad (2)$$

that is, the logarithm of the yield of furfural is a linear function of the concentration of salt and also of pH.

Equation 2 was applied to all the hydrochloric acid-sodium chloride systems; these values are given as f_1 in table 4. The agreement is entirely satisfactory through ranges in which the yield of furfural is a linear function of the "apparent" hydrogen-ion concentration. In general the relation is linear up to about 22 per cent yield of furfural. This treatment permits the calculation of yields below 10 per cent, which are somewhat erratic owing to the low concentrations in the toluene.

Graphs of pH against furfural yield (f_1) for the 0.25 *N* hydrochloric acid-salt combinations for the 2-, 4-, and 6-hour periods permitted the calculation of the pH of other concentrations of pure acid, on the assumption that the yield of furfural is a function of pH only. Such values are given in table 5. There are also included data for various concentrations of hydro-

TABLE 5

The pH values of 0.50 N, 0.75 N, 1.00 N, 1.50 N, and 2.00 N hydrochloric acid as calculated on basis of yields with 0.25 N hydrochloric acid-sodium chloride systems, compared to pH values as calculated from the activity coefficient of hydrochloric acid

CONCENTRATION OF HCl		pH FROM GRAPH FURFURAL YIELD FOR 0.25 N HCl-NaCl				pH FROM VALUES OF γ HCl				
Molar	Molal	2 hrs	4 hrs.	6 hrs.	Average	γ	Relative value of γ	$\gamma'm$	$\text{pH}_1 = \log \frac{1}{\gamma'm}$	$\text{pH} - \text{pH}_1$
0.25	0.25					0.761	1	0.25	0.60	0
0.50	0.50	0.29	0.27	0.26	0.27	0.757	0.995	0.50	0.30	-0.03
0.75	0.76	0.04	0.09	0.09	0.07	0.780	1.03	0.78	0.11	-0.04
1.00	1.02	-0.02	-0.02	+0.01	-0.01	0.815	1.07	1.09	-0.04	+0.03
1.50	1.54	-0.24	-0.23		-0.24	0.901	1.18	1.82	-0.26	+0.02
2.00	2.08	-0.50	-0.40		-0.45	1.04	1.37	2.85	-0.45	0

TABLE 6

*Values of pH of various combinations of sodium chloride and hydrochloric acid**

PER CENT NaCl	NORMALITY OF HCl					
	0.25	0.50	0.75	1.00	1.50	2.00
0	0.60	0.27	0.07	-0.01	-0.24	-0.45
5	0.46	0.13	-0.07	-0.15	-0.38	-0.59
10	0.32	-0.01	-0.21	-0.29	-0.52	-0.73
15	0.50	-0.15	-0.35	-0.43	-0.66	-0.87
20	0.04	-0.29	-0.49	-0.57	-0.80	-1.04
25	-0.10	-0.43	-0.63	-0.71	-0.94	-1.18
30	-0.24	-0.57	-0.77	-0.85	-1.08	-1.32
35	-0.38	-0.71	-0.91	-0.99	-1.22	-1.46
40	-0.52	-0.85	-1.05	-1.13	-1.36	-1.60
45	-0.66	-0.99	-1.19	-1.27	-1.50	-1.74

* Data for 0.25 *N* hydrochloric acid based on experimental data from the relation, $\text{pH} = 0.60 - 0.028 \times \text{per cent NaCl}$. Data for other concentrations calculated from table 5, using the relation $\text{pH} = b - 0.028 \times \text{per cent NaCl}$.

chloric acid calculated from the activity coefficients given by Randall and Young (17). Our value for 0.25 *N* hydrochloric acid is $\text{pH} = 0.60$ as compared to 0.71 calculated from the activity coefficient. Relative values of the activity coefficients, γ' , were used to correct our values to the basis of the data of Randall and Young. It is evident that the pH values

calculated from yields of furfural in the presence of the pure acid agree remarkably well with those calculated from the activity coefficients.

It was noted above that equation 2 applies, within specified limits, to all combinations of hydrochloric acid and sodium chloride. The assumption seems warranted that the pH of other concentrations of acid decreases at the same rate as obtained for 0.25 *N* hydrochloric acid, that is,

$$\text{pH} = b - 0.028 \times \text{per cent NaCl} \quad (3)$$

Values so calculated are given in table 6.

Graphs were constructed by plotting $\log f$ against pH for the 2-, 4-, 6-, and 8-hour periods. Each curve included all the data for all combinations of hydrochloric acid and sodium chloride for the given period. From these graphs the furfural yield for each pH value was read. The data so obtained are given as f_2 in table 4. It is evident that, within experimental accuracy, the yield of furfural from 20 per cent xylose solution in the presence of hydrochloric acid-sodium chloride combinations is determined by the pH values of the wide variety of combinations employed.

V. SUMMARY

Studies are reported on the production of furfural from strong xylose solutions using hydrochloric acid-sodium chloride solutions as dehydrating agents. The xylose-hydrochloric acid-sodium chloride systems were refluxed, at atmospheric pressure, with toluene. The furfural yield was determined from the specific gravities of the resulting furfural-toluene solutions. The concentrations of hydrochloric acid used were 0.25, 0.50, 0.75, 1.00, 1.50, and 2.00 normal, each in the presence of 0, 5, 10, 15, 20, 25, 30, 35, 40, and 45 per cent sodium chloride. The yield of furfural was twice as great for 4 per cent xylose as for 60 per cent xylose. Detailed experiments were performed for xylose at 20 per cent concentration for which the yield in furfural is about 20 per cent less than for 4 per cent xylose.

The yield of furfural is increased about one-third for each 5 per cent addition of sodium chloride up to a furfural yield of about 22 per cent. From this point the increase in yield is less. For all cases, for a given time period, the yield of furfural is, within reasonable limits, dependent only upon the pH of the hydrochloric acid-sodium chloride combinations. That is, the yield is dependent upon the thermodynamic degree of dissociation of the acid (the activity coefficient).

REFERENCES

- (1) ADAMS AND VORHEES: *Organic Syntheses*, Collective Volume, p. 274. John Wiley and Sons, Inc., New York (1932).
- (2) ÅKERLÖF: *Z. physik. Chem.* **98**, 260 (1921).

- (3) BOWE: J. Phys. Chem. **31**, 291 (1927).
- (4) BRÜNSTED: Trans. Faraday Soc. **24**, 630 (1928).
- (5) BROWNLEE: Ind. Eng. Chem. **19**, 422 (1927).
- (6) BUCHANAN AND FULMER: Physiology and Biochemistry of Bacteria, Vol. I, p. 262 (1928); Vol. II, p. 234 (1930). The Williams & Wilkins Co., Baltimore.
- (7) COLIN AND CHAUDIN: Compt. rend. **192**, 1229 (1931).
- (8) DAWSON: Trans. Faraday Soc. **24**, 640 (1928).
- (9) FLOYD: J. Phys. Chem. **35**, 2968 (1931).
- (10) HARNED AND ÅKERLÖF: Trans. Faraday Soc. **24**, 666 (1928).
- (11) HUNTER: J. Chem. Soc. **1928**, 2643.
- (12) HURD AND ISENHOUR: J. Am. Chem. Soc. **54**, 317 (1932).
- (13) HURD AND ISENHOUR: J. Am. Chem. Soc. **54**, 693 (1932).
- (14) KILLEFER: Ind. Eng. Chem. **18**, 1217 (1926).
- (15) KLINE AND ACREE: Bur. Standards J. Research **8**, 25 (1930).
- (16) MINER, TRICKEY, AND BROWNLEE: Chem. Met. Eng. **27**, 299 (1922).
- (17) RANDALL AND YOUNG: J. Am. Chem. Soc. **50**, 989 (1928).
- (18) SHAFFER AND HARTMANN: J. Biol. Chem. **45**, 365 (1920).
- (19) SLATER AND ACREE: Ind. Eng. Chem., Anal. Ed. **2**, 274 (1930).
- (20) TERRY: J. Am. Chem. Soc. **50**, 1239 (1928).

A METHOD FOR THE DETERMINATION OF THE WALL CORRECTION FOR THE FALLING SPHERE VISCOMETER¹

ELLIS I. FULMER AND JOHN C. WILLIAMS

Department of Chemistry, Iowa State College, Ames, Iowa

Received July 8, 1935

INTRODUCTION

The use of the simple Stokes' equation in the determination of viscosity rests upon a number of assumptions. According to Arnold (3) these are: (a) there is no slip between the medium and the surface of the sphere; (b) the velocity of fall is small; (c) the sphere is rigid; (d) the discontinuities of the medium are small, compared to the size of the sphere; and (e) the liquid is infinite in extent.

The cylinder containing the liquid is immersed in a constant-temperature bath and fixed in an accurately vertical position. The sphere is introduced axially into the liquid by means of a glass tube passing through a stopper at the top of the cylinder. Ladenburg (8) released the sphere beneath the surface by means of an electromagnet. The velocity of fall is determined over the middle third of the liquid column; the timing lines should extend around the cylinder in order to avoid parallax. The liquid must be free from gas bubbles and convection currents. Lemin (9) found in measuring the viscosity of glycerol, that it was necessary to wait ten minutes between the passage of the spheres in order to obtain consistent results. The requirement of spheres is easily met by the use of ball-bearings, which are made in standard sizes with an accuracy of 0.001 inch. Ladenburg (8) found the velocity of fall of spheres with corroded surfaces to be identical with that for spheres with polished surfaces. Lemin (9) stated that with very small spheres the slippage must be taken into account, but that this factor is not significant with sphere sizes employed in the laboratory viscometer. Gibson and Jacobs (7), Poynting and Thomson (11), and Allen (1) have emphasized the fact that there is a lower limit to the viscosity which can be measured with the falling sphere viscometer and an upper limit of the size of the sphere which can be employed using the simple Stokes' equation.

¹ This work was supported in part by a grant from the Industrial Science Research funds of the Iowa State College for the study of the granulation of honeys.

The simple Stokes' law may be formulated as

$$\eta = \frac{2(d_1 - d_2)gr^2}{9v} \quad (1)$$

in which v = velocity of fall, d_1 = density of sphere, d_2 = density of the medium, η = absolute viscosity of the medium, r = radius of the sphere, and g = the gravity constant.

It is evident that the extent of the liquid and the height of the column of liquid are factors in the rate of fall of the sphere. Ladenburg (8) applied two linear equations to the simple Stokes' law to correct for variations in the extent of the liquid and for the height of the liquid column. His correction for the "wall effect" is

$$v(1 + 2.4r/R) = v_\infty \quad (2)$$

in which v is the observed velocity, v_∞ the velocity in infinite medium, r the radius of the sphere, and R the inside radius of the cylinder. The above relation has been verified, within limits, by Gibson and Jacobs (7), Lemin (9), and others. Lemin found the relation to hold for values of r/R up to 0.06.

The correction for the "end effect" is

$$v(1 + 3.3r/h) = v_\infty \quad (3)$$

in which h is the height of the column of liquid.

Sheppard (13) derived an empirical equation in an endeavor to extend the wall correction to wider ranges of r/R . His relation is

$$T = T_\infty + \frac{C}{(R/r - 1)^2} \quad (4)$$

in which T is the observed time of fall, T_∞ the time of fall in infinite medium, and C a constant. With reference to the above equation Gibson and Jacobs (7) state, "Although the expression may fit the author's data when suitable constants are chosen, this does not prove that the value of T_∞ is the correct one."

Equation 4 may be written,

$$\log(T - T_\infty) = -2 \log(R/r - 1) + \log C \quad (5)$$

The above equation was applied graphically to the data of Lemin (3) (see table 2) for the viscosity of glycerol. The value of T_∞ so obtained gave a viscosity of 20.5 poises. This is higher than the three lowest values given by Lemin and 2 poises higher than the value using Ladenburg's correction.

Gibson and Jacobs (7) suggested that the viscometer should be calibrated by using a liquid of known viscosity; they employ the relation,

$$\frac{\eta_1}{\eta_2} = \frac{(d_1 - d_2)T_1}{(d_1 - d_3)T_2} \quad (6)$$

In regard to the above equation Bingham (4) states: "Workers have felt dependent upon calibrating liquids, and since there is a dearth of calibrating liquids of high viscosity, liquids are often chosen in which the velocity of fall is too great for strict application of Stokes' law and a correction has to be made."

The work here was undertaken during the course of studies on various properties of honeys as correlated with their tendency to granulate (6). Chataway (5) found the water content of honeys to be correlated with viscosity as determined by the falling sphere viscometer and gives tables for this purpose. The value of r/R for his viscometer was 0.317, which involves a large correction factor. He points out in a second communication that his tables apply only for a viscometer of the same dimensions as employed by him.

The determination of the viscosity of honeys is complicated by the fact that some samples have been shown to exhibit an anomalous behavior. For example, deBoer and Knipphorst (2) found the viscosity of heather honey to be decreased by stirring, with subsequent increase in viscosity on standing. They describe the phenomenon as an example of thixotropy. Paine, Gertler, and Lothrop (10) noted that certain honeys show a slight decrease in viscosity with increase in stress. Scott Blair (12) made detailed studies of the thixotropy of heather honey under shearing in both its undisturbed ("gel") and stirred ("sol") forms. In both cases, the viscosity increased at low stresses, but in neither case was there found any sharp elastic limit (yield value). The sol form showed (considering its high viscosity) only a very small deviation from truly fluid behavior." He describes a viscometric test to characterize honeys having thixotropic properties.

EXPERIMENTAL

In tables 1 to 6 are given data for the viscosities of various liquids with various values of r/R and h . The data for castor oil, glycerol, and a system of colophony-turpentine are adapted from the literature, while those for a system of colophony-turpentine and for two honeys were determined in these laboratories. It was found that, within limits, the determined viscosity is an exponential function of r/R such that,

$$\log (\eta_x - b) = mr/R + \log (\eta_\infty - b) \quad (7)$$

TABLE 1

*Viscosity of castor oil at 20°C.*Calculated from data of Gibson and Jacobs (7). $h = 25.5$; $r = 0.0794$

R^*	r/R	η_z	η'_z	η_∞	η_L
2.270	0.0350	10.66	10.55	9.91	9.73
1.750	0.0454	10.84	10.73	9.89	9.67
1.050	0.0756	11.51	11.39	9.85	9.64
1.000	0.0794	11.88	11.76	10.09	9.88
0.570	0.1395	13.35	13.21	9.79	9.89
0.425	0.1870	15.43	15.27	9.89	10.54

* In this and the following tables r = radius of sphere, R = inside radius of cylinder, η_z = viscosity calculated by simple Stokes' law, η'_z = viscosity corrected for end effect by Ladenburg equation 3, η_∞ = viscosity for infinite liquid calculated by equation 11, η_L = viscosity for infinite liquid calculated by Ladenburg equation 2.

TABLE 2

*Viscosity of glycerol at 12°C.*From data of Lemin (9). $h = 30.0$; $r = 0.0794$

R	r/R	η_z	η'_z	η_∞	η_L
4.84	0.0164	19.0	18.8	18.3	18.1
2.90	0.0274	20.3	20.1	19.2	18.9
2.35	0.0338	20.2	20.0	18.9	18.5
1.70	0.0467	20.6	20.4	18.8	18.4
1.43	0.0557	21.1	20.9	18.9	18.5
1.30	0.0610	21.3	21.1	18.9	18.4
0.860	0.0923	22.7	22.6	18.8	18.4
0.435	0.1825	29.8	29.5	19.4	20.5
0.280	0.2835	37.3	37.0	17.3	22.0

TABLE 3

Viscosity of colophony-turpentine

From data of Ladenburg (8)

r/R	r/h	η_z	η'_z	η_∞	η_L
0.0107	0.00312	1396	1382	1357	1347
0.0141	0.00414	1415	1396	1363	1348
0.0189	0.00312	1424	1409	1364	1349
0.0213	0.00625	1438	1409	1358	1338
0.0249	0.00414	1447	1427	1367	1344
0.0283	0.00826	1456	1417	1348	1328
0.0340	0.00312	1490	1475	1389	1362
0.0376	0.00625	1491	1461	1394	1340
0.0450	0.00414	1515	1494	1368	1349
0.0500	0.00826	1515	1475	1347	1318
0.0680	0.00625	1600	1568	1378	1346
0.0901	0.00826	1681	1636	1379	1348

TABLE 4
Viscosity of colophony-turpentine at 25°C.

R	r	r/R	h	η_x	η_x'	η_∞	η_L
2.15	0.1587	0.074	33	75.3	74.1	64.3	62.9
2.15	0.2381	0.111	33	84.0	82.4	65.7	65.1
2.15	0.3170	0.147	33	95.9	92.9	67.5	68.7
2.15	0.3970	0.185	33	102.9	98.9	64.4	68.5
0.55	0.1181	0.215	22	115.7	113.7	67.5	75.0
2.15	0.5000	0.232	33	121.7	115.9	65.0	74.4
0.55	0.1587	0.288	22	150.5	147.0	67.6	86.9
2.15	0.6350	0.295	33	150.9	141.9	63.6	83.1
0.55	0.2381	0.433	22	274.7	265.2	66.6	130.6
0.55	0.3170	0.576	22	645.6	616.3	77.6	258.7

TABLE 5
Viscosity of holly honey at 25°C.

R	r	r/R	h	η_x	η_x'	η_∞	η_L
2.15	0.1181	0.055	33	238.1	235.3	212.6	207.8
2.15	0.1587	0.074	33	249.1	245.2	212.1	208.2
2.15	0.2381	0.111	33	265.1	258.9	206.4	204.4
2.15	0.3170	0.147	33	285.5	276.7	201.1	204.5
2.15	0.3970	0.185	33	306.0	294.3	191.8	203.8
2.15	0.5000	0.232	33	367.2	349.7	196.4	224.6
2.15	0.6350	0.295	33	451.2	424.2	190.1	248.4

TABLE 6
Viscosity of sourwood honey at 25°C.

R	r	r/R	h	η_x	η_x'	η_∞	η_L
2.15	0.1181	0.055	33	73.7	72.7	65.7	64.3
2.15	0.1587	0.074	33	76.8	75.5	65.5	64.1
1.25	0.1181	0.095	30	79.2	78.2	64.8	63.7
2.15	0.2380	0.111	33	85.2	83.2	66.3	65.7
1.25	0.1587	0.127	30	89.0	87.4	66.9	66.9
2.15	0.3170	0.147	33	95.1	92.2	67.0	68.1
2.15	0.3970	0.185	33	104.3	100.2	65.3	69.4
1.25	0.2381	0.191	30	107.0	104.2	66.8	71.6
2.15	0.5000	0.232	33	121.3	116.6	65.4	74.9
1.25	0.3170	0.254	30	126.7	122.4	64.4	76.0
2.15	0.6350	0.295	33	150.1	141.2	63.3	82.6
1.25	0.3970	0.318	30	156.2	149.7	61.3	84.9
1.25	0.5000	0.400	30	216.0	204.8	59.6	104.5
1.25	0.635	0.508	30	372.1	347.8	61.3	156.6

in which η_x is the determined viscosity, η_∞ the viscosity in liquid of infinite extent, and b is a constant.

Equation 7 may be written as,

$$\frac{\eta_x - b}{\eta_\infty - b} = 10^{mr/R} \quad (8)$$

While there was some variation in the value of m , the average value was 2.4, which is identical with the factor in the Ladenburg equation (equation 3) for correction for the wall effect.

It was also found that b is proportional to η_∞ , or,

$$b = 0.700\eta_\infty \quad (9)$$

Substituting in equation 8

$$\frac{\eta_x - 0.7\eta_\infty}{\eta_\infty - 0.7\eta_\infty} = 10^{2.4r/R} \quad (10)$$

and,

$$\frac{\eta_x}{\eta_\infty} = 0.3 \times 10^{2.4r/R} + 0.7 \quad (11)$$

A table of values of $0.3 \times 10^{2.4r/R}$ as a function of r/R permitted the calculation of η_∞ for the data in tables 1 to 6. Somewhat more concordant results were obtained by making a correction for end effect, using equation 3 (Ladenburg's). These values are given as η_x' . Values are also given for η_∞ as calculated by equation 11 and by means of Ladenburg's equation (equation 2) for correction for the wall effect. It is at once evident that while the Ladenburg equation is valid up to a value of r/R of about 0.100, equation 11 gives concordant results up to a value of r/R of about 0.500. Through the range of validity of Ladenburg's equation, the two methods of calculation agree within reasonable limits. It should also be noted that the values for η_∞ for the honeys, as calculated by means of equation 11, show some tendency to decrease with increase in r/R . This drift is in harmony with the thixotropic properties of honeys as previously discussed.

SUMMARY

An equation has been derived by means of which the wall correction for the falling sphere viscometer can be made for values of r/R up to about 0.500.

REFERENCES

- (1) ALLEN: *Phil. Mag.* [5] **50**, 323 (1900).
- (2) DE BOER AND KNIPHORST: *Chem. Weekblad* **29**, 526 (1932).
- (3) ARNOLD: *Phil. Mag.* [6] **22**, 755 (1911).

- (4) BINGHAM: Fluidity and Plasticity, p. 329. McGraw-Hill Book Co., New York (1922).
- (5) CHATAWAY: Can. J. Research **6**, 532 (1932); **8**, 435 (1933).
- (6) FULMER, BOSCH, PARK, AND BUCHANAN: Am. Bee J. **12**, 208 (1934).
- (7) GIBSON AND JACOBS: J. Chem. Soc. **117**, 473 (1920).
- (8) LADENBURG: Ann. Physik **23**, 447 (1907).
- (9) LEMIN: Phil. Mag. [7] **12**, 589 (1931).
- (10) PAINE, GERTLER, AND LOTHROP: Ind. Eng. Chem. **26**, 73 (1934).
- (11) POYNTING AND THOMSON: Properties of Matter, p. 222. Chas. Griffen, London (1919).
- (12) SCOTT BLAIR, G. W.: J. Phys. Chem. **39**, 213 (1935).
- (13) SHEPPARD: Ind. Eng. Chem. **9**, 523 (1917).

THE EFFECT OF CERTAIN SUGAR ALCOHOLS AND THEIR ANHYDRIDES ON THE DISSOCIATION OF BORIC ACID

JOHN C. KRANTZ, JR., MARGARETHE OAKLEY, AND C. JELLEFF CARR

*Department of Pharmacology, School of Medicine, University of Maryland,
Baltimore, Maryland*

Received June 20, 1935

INTRODUCTION

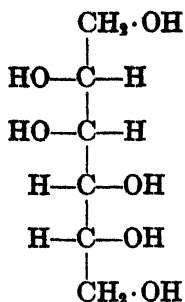
The use of the polyhydric alcohols in the titration of boric acid with alkalis is a well-established analytical procedure. The increase of the dissociation constant of the acid in the presence of various polyhydric alcohols and phenols was studied extensively by Böesecken (1). The subject was studied further and comprehensively reviewed by Mellon and Norris (2). The authors became interested in the fate of certain sugar alcohols and their anhydrides in the animal body (3, 4) and in bacterial culture media (5). The differences in effect were so striking that a comparison of the influences of these substances on the titration curves of boric acid suggested itself. Previously van Romburgh and van der Burg (6) have measured the difference between the electrical conductivity of boric acid in mannitol, mannitan, and isomannide solutions.

MATERIALS

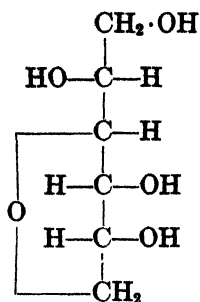
The mannitol used in this investigation was supplied through the courtesy of Merck and Company, Inc., Rahway, N. J. The aqueous solution of the compound (1:10) is neutral to litmus and very slightly dextrorotatory. The mannitan was prepared from mannitol by a slight modification of the method of Vignon (7), in which the dehydration is accomplished by means of sulfuric acid. The compound was acetylated and the resulting ester distilled *in vacuo*. The fraction distilling between 200–210°C. at 10 mm. was saponified. The calculated percentage of acetic acid is 72.31; that found was 71.70. The mannide was prepared by the method devised by Liebermann (8). Analysis gave: C, 48.37 per cent; H, 7.32 per cent. The calculated values are: C, 49.27 per cent; H, 6.90 per cent. The isomannide was prepared by Fauconnier's method (9). The compound melted sharply at 87°C. (uncorrected).

The dulcitol employed was Pfanstiehl's c.p. product, m.p. 188°C., free from galactose. The dulcitan was prepared by Berthelot's method (10). Analysis gave the following composition: C, 43.79 per cent; H, 7.20 per cent. The calculated values are: C, 43.87 per cent; H, 7.37 per cent.

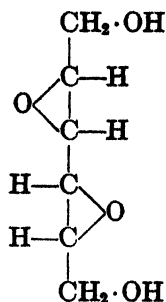
The following formulas indicate the structural relationships existing among the compounds.



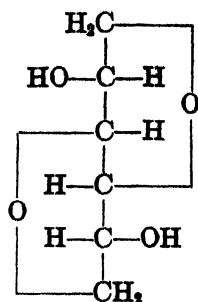
Mannitol



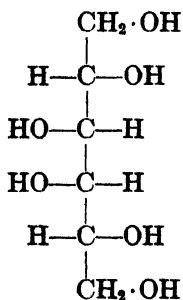
Mannitan



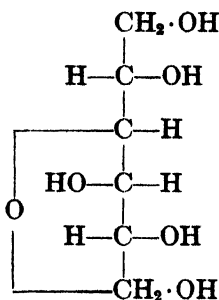
Mannide



Isomannide



Dulcitol



Dulcitan

METHOD

The solutions of the various compounds used contained 4 g. of compound in 100 cc. of 0.1 molar boric acid. To 10-cc. portions was added 0.1 normal sodium hydroxide in quantities varying from 1 cc. to 11 cc. Immediately after the addition of the alkali the pH of the solution was determined electrometrically at $25 \pm 0.5^\circ\text{C}$., using a Wilson (11) type hydrogen electrode. The results are set forth in figure 1.

DISCUSSION

It will be observed that the two hexahydric alcohols have practically the same dissociation-potentiating capacity on solutions of boric acid. The second anhydride of mannitol, namely isomannide, with two ring structures in the molecule, does not possess the capacity to influence the dissociation of boric acid, and the titration curve for the acid containing isomannide is practically identical with that of the acid alone. The curves for the two first anhydrides lie intermediate between the values obtained for the alcohols and those obtained for pure boric acid.

The curve for the double anhydride of mannitol, mannide, shows this

substance to have a greater potentiating influence on the dissociation of boric acid than the first anhydrides. A comparison of this fact with the structure assigned to mannide by Liebermann (8) is incompatible with the hypothesis of Böeseken (1), namely, that the strongly dissociating complexes of boric acid are formed when two hydroxyl groups are situated on the same side of adjacent carbon atoms to which they are bound. The authors observed the rather rapid conversion of mannide into mannitol in the presence of alkali. It is possible that the partial conversion of this

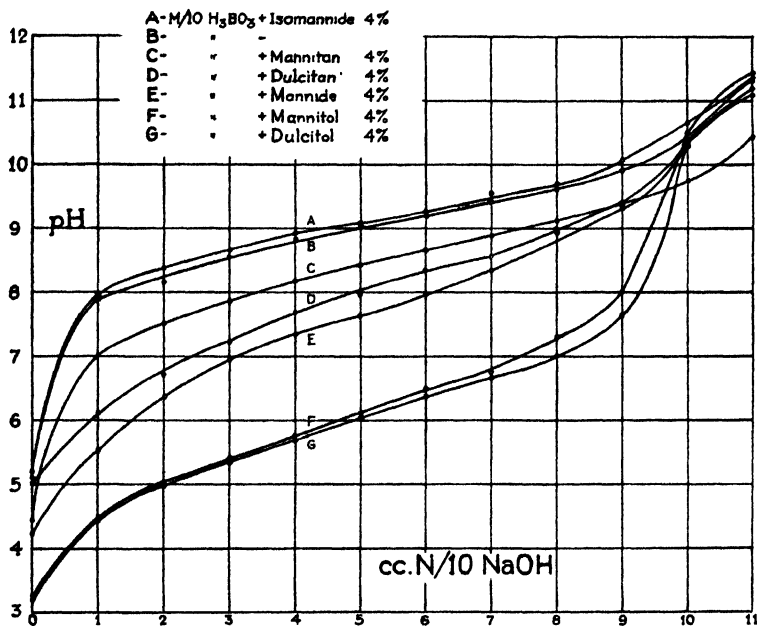


FIG. 1. Titration curves of boric acid in the presence of certain sugar alcohols and their anhydrides

double anhydride into the polyhydric alcohol is responsible for the observed effect on the titration curve.

SUMMARY

The influence of two polyhydric alcohols, mannitol and dulcitol, on the titration curve of boric acid has been studied. This effect has been compared with the action of the anhydrides mannitan, mannide, isomannide, and dulcitan.

REFERENCES

- (1) BÖESEKEN: *Rec. trav. chim.* **40**, 553 (1921).
- (2) MELLON, M. G., AND NORRIS, V. N.: *Ind. Eng. Chem.* **16**, 123 (1924).

- (3) CARR, C. J., MUSSEY, R., SCHMIDT, J. E., AND KRANTZ, J. C., JR.: J. Biol. Chem. **102**, 721 (1933).
- (4) CARR, C. J., AND KRANTZ, J. C., JR.: J. Biol. Chem. **107**, 371 (1934).
- (5) DOZOIS, E. P., HACHTEL, F., CARR, C. J., AND KRANTZ, J. C., JR.: In press.
- (6) VAN ROMBURGH, G., AND VAN DER BURG, J. H. N.: Proc. Acad. Sci. Amsterdam **25**, 335 (1922).
- (7) VIGNON, L.: Ann. chim. phys. [5] **2**, 458 (1874).
- (8) LIEBERMANN, C.: Ber. **17**, 874 (1884).
- (9) FAUCONNIER, A.: Bull. soc. chim. Paris **41**, 119 (1884).
- (10) BERTHELOT, M.: Chimie organique sur la synthese, Paris, **2**, 209 (1860).
- (11) WILSON, J. A.: Ind. Eng. Chem. **17**, 74 (1925).

THE RADIOCHEMICAL DECOMPOSITION OF DEUTERO-AMMONIA

J. C. JUNGERS¹

School of Chemistry, University of Minnesota, Minneapolis, Minnesota

Received July 18, 1935

INTRODUCTION

The study of the mercury photosensitized decomposition of the ammonias at room temperature (2) showed that under comparable conditions ammonia decomposes eleven times faster than the ammonia-d₃. Part of this ratio can be ascribed to the lower quenching power of deuterio-ammonia; this fact taken into account brings the decomposition ratio to 5. This corresponds to a difference in activation energy of 950 calories (1).

It has been shown that the rates of decomposition on a hot tungsten wire yield the ratio 1.6:1, corresponding to a difference in activation energy of 900 calories (3).

It was considered of interest to find out how this difference in activation energy would affect the radiochemical reaction.

EXPERIMENTAL DETAILS

For this study the method of central irradiation was chosen. This allows both numerous runs and comparable conditions. The α -ray bulb was mounted in the center of a 100-cc. sphere in which the gases were submitted to irradiation. The gases produced by decomposition were pumped off, after the undecomposed ammonia had been frozen out, and measured in a Ramsay gauge. The ammonia could then be vaporized and a new run started, the same sample being used throughout the series of runs. The first run was systematically discarded. Because the decrease in pressure due to the removal of the products of decomposition is very small (about 1/1000 of total pressure), the experiments can be considered as carried out at the same pressure.

It was not judged necessary to measure the emanation, because only relative values were wanted. The activity of all the bulbs used was of the order of 50 millicuries.

For the runs at 20°C. the temperature was controlled by keeping the reaction vessel in a large Dewar flask filled with water. For the runs at

¹ C. R. B. Fellow from the University of Louvain to the University of Minnesota.

100°C. and 184°C. the vessel was kept in steam and aniline vapor, respectively.

The gases used in these experiments were prepared by passing H_2O and D_2O over magnesium nitride, obtained by interaction of purified nitrogen and magnesium at 700°C. The deuterium content of the hydrogen in the two samples of heavy ammonia submitted to reaction was 68 per cent and 98 per cent. The last sample analyzed spectrographically before and after a long irradiation did not reveal a difference in deuterium concentration.

DATA

Influence of temperature

The data on the decomposition of ammonia and deuterio-ammonia are given in table 1. The first column gives the nature and the pressure at 20°C. of the gas submitted to reaction. The temperature at which the

TABLE 1
Decomposition of ammonia and of deuterio-ammonia

PRESSURE IN MM.	T IN °C.	E	ΔE	ΔP	R
NH ₃					
52.5	20	64558	2446	5.33	218
	20	61648	3373	7.42	222
	20.3	57814	3914	8.76	224
	22	53239	4418	10.12	229
	100	48284	2182	9.11	418
	100	45442	2129	8.85	416
	100	42797	1904	7.91	415
	184				580
ND ₃					
52.6	100	36381	2378	6.67	281
	20.7	33647	2830	4.92	174
	100	30333	1694	4.86	286
	22.1	28437	2810	5.03	179
	100	25337	1810	5.18	281
	20.5	23283	2535	4.49	177
	184	20603	2601	9.21	354

experiments were carried out is given in the second column. The emanation E , present at the beginning, and the emanation ΔE decayed during the reaction are given in the third and fourth columns. These data are obtained from Kolowrat's table, the sealing of the bulb being taken as origin. The pressure ΔP of the decomposed gases measured in a volume of 2 cc. is recorded in the fifth column. The sixth column shows the rate of decomposition $\Delta P/\Delta E = R$. The value of R for the decomposition of ammonia at 184°C. is obtained by extrapolation of Wourtzell's curve, with which

our results at 20°C. and 100°C. are in perfect agreement. These data yield the following values for the ratios of the rates of decomposition.

T in °C.....	20	100	184
R_{NH_3}/R_{ND_3}	1.27	1.47	1.64

Influence of the concentration of D_2

A sample of ammonia containing 68 per cent deuterium compared with the ordinary ammonia yielded the data contained in table 2. The columns

TABLE 2
Decomposition of ammonia containing 68 per cent deuterium

PRESSURE IN MM	T IN °C	E	ΔE	ΔP	R
NH ₃					
54.9	20.2	92600	6582	11.98	182
	20.0	84926	4490	8.07	179
	20.4	78782	6574	11.90	187
R					181
ND ₃					
54.75	20	62462	3232	4.92	152
	22	58275	2977	4.52	152
	21	54567	5034	7.86	154
R					153

have the same significance as in table 1. These data in connection with those of table 1 give the variation of the rate of reaction with concentration in D_2 .

Concentration in per cent.....	0	68	98
$R_{NH_3}/R_{N(H_xD_y)_3}$	1	0.84	0.79

These data show a practically linear relationship between the rate and the deuterium concentration.

DISCUSSION

The rate of decomposition $\Delta P/\Delta E$ is a function of the stopping power, the specific ionization, and the ion yield,

$$V = \frac{\Delta P}{\Delta E} C \left[S, K, \frac{M}{I} \right]$$

C is a constant independent of the nature of the gas. All these data are well known for ordinary ammonia. A very careful determination of the

ion yield has been made by A. Luyckx (5). In the case of the deuterio-ammonias S can be determined by Glasston's law, giving the stopping power as a function of the atomic number: this gives $S_{NH_3} = S_{ND_3}$. No determination of k_{ND_3} has yet been made, but as the specific ionization varies for simple compounds between rather restricted limits one can consider the specific ionization of proto-ammonia and deuterio-ammonia as being practically equal. The fact that the rate of polymerization is the same for proto-acetylene and acetylene- d_2 (4) seems to justify this assumption. It is thus safe to admit that the ion yields are very closely in the same ratio as the rate of reaction. The fact that this ratio, close to one at low temperature, rises with increasing temperature is in striking contrast with the reactions where the rate of reaction is determined by the activation energy. It has been shown that the photochemical reaction of ammonia is a component of decomposition and partial recombination. This is most probably also the case in the radiochemical reaction. The lower ion yield, and especially its slower rise with temperature, cannot be ascribed to a more efficient recombination in the case of ammonia- d_3 , its activation of formation being higher than for ordinary ammonia. The lower ion yield has thus to be ascribed to the decomposition process itself.

No satisfactory explanation is at hand, but the increase in ion yield with temperature for both ammonias points towards a chain-like mechanism, which is best explained by admitting the clusters formed by the molecules around an ion as reaction center. It is likely that it is the difference in growth in this chain, determined by the activation energy of the decomposition, which controls the ratio of the reaction rates.

SUMMARY

The rate of decomposition of ammonia- d_3 was compared with the rate of decomposition of ordinary ammonia and found to be inferior, to rise more slowly with increasing temperature, and, at constant temperature, to increase with decreasing deuterium content.

I wish to express my heartiest thanks to Professor S. C. Lind, Director of the School of Chemistry of the University of Minnesota, for his advice and for placing his laboratory and the necessary amount of radon at my disposal. My thanks go also to Professor Hugh S. Taylor of Princeton University for kindly supplying me with the necessary quantity of deuterium oxide.

REFERENCES

- (1) EVANS, M. G., AND TAYLOR, H. S.: J. Chem. Physics **2**, 732 (1934).
- (2) JUNGERS, J. C., AND TAYLOR, H. S.: J. Chem. Physics **2**, 373 (1934).
- (3) JUNGERS, J. C., AND TAYLOR, H. S.: J. Am. Chem. Soc. **57**, 679 (1935).
- (4) LIND, S. C., JUNGERS, J. C., AND SCHIFFLETT, C. H.: J. Am. Chem. Soc. **57**, 1032 (1935).
- (5) LUYCKX, A.: Bull. soc. chim. Belg. **43**, 117 (1934).

THE DETERMINATION OF CONTACT ANGLES FROM MEASUREMENTS OF THE DIMENSIONS OF SMALL BUBBLES AND DROPS. I

THE SPHEROIDAL SEGMENT METHOD FOR ACUTE ANGLES¹

GUILFORD L. MACK

*Division of Chemistry, New York State Agricultural Experiment Station,
Geneva, New York*

Received January 11, 1935

INTRODUCTION

The present methods of measuring contact angles all require that the solid material be obtainable in some special shape, such as a flat plate or capillary tube. Many surfaces, for example, those of plant materials, occur in irregular forms and must be dealt with *in situ*, because of the inhomogeneity of the body. The chief value of the method herein described is that its applicability is largely independent of the form of the solid surface.

Some of the earliest determinations of contact angles were made from measurements of the dimensions of bubbles and drops. The work has been confined to large drops, but the use of very small drops may be shown to possess several advantages: (1) Small drops may be applied successfully to small plane areas in an irregular surface or even to surfaces with an approximately constant degree of curvature. (2) Small drops show a much greater variation in height for small variations in magnitude of contact angle than do large drops. Accordingly, this dimension does not have to be measured with such extreme accuracy as is necessary with large drops. (3) Small drops assume the advancing angle of contact, while larger drops exhibit a fluctuating angle of contact varying roughly between the advancing and receding angles.

Other generally applicable means of measuring contact angles are the various modifications of the tilting plate method (1), and methods depending upon visual observation of the image of a drop, bubble, or meniscus projected upon a screen or photographic plate (7, 8, 3). It may be noted that in each of these methods the contact angle is measured at a single point on the surface. Such a procedure is somewhat unsatisfactory for

Approved by the Director of the New York State Agricultural Station for publication as Journal Paper No. 44.

working with naturally occurring objects having variable surface properties. The proposed method has the advantage of yielding a value for the contact angle which is the integral of the sum of all the separate angles along the circumference of the drop.

THEORY OF THE SPHEROIDAL SEGMENT METHOD

The principle of the spheroidal segment method is based upon the fact that the shape of a small drop of liquid having an acute angle of contact is only slightly affected by the influence of gravity. Consequently, the surface will be nearly spherical, and as a first approximation the drop may be considered to be a segment of a sphere.

The angle between the horizontal plane through the base of the drop and the tangent to the spherical surface at the point of contact is

$$\theta = 2 \tan^{-1} (h/x) \quad (1)$$

where h is the greatest height of the drop and x is the radius of the base of segment. The distance x is easily measured on a scale in the eyepiece of a low power microscope, but the value of h is usually much smaller and more difficult to measure. This is especially true in the case of small angles on a surface which is not perfectly plane. Another difficulty is the fact that small drops evaporate very rapidly if the surrounding vapor is not in equilibrium, a condition which is difficult to accomplish and even more difficult to maintain.

The problem may be solved by substituting the volume for the height as a measurable dimension of the drop. The volume of a number of equally formed drops may be measured in an auxiliary reservoir and such measurements will be entirely independent of the shape of the solid surface. Furthermore, the volume measurement is made at the time the drop is first formed and is unaffected by subsequent changes caused by evaporation. It was observed experimentally that an evaporating drop maintained its original radius long after its other dimensions, such as height, volume, and contact angle, had been considerably reduced.

Thus from an experimental point of view, it appeared highly desirable to determine the contact angle from measurements of the radius and volume of the drop. This may be done by expressing the value of h in equation 1 as a function of the radius and volume of a spherical segment. The equation relating these quantities is

$$h^3 + 3hx^2 = 6(V/\pi) \quad (2)$$

No simple algebraic expression for h in terms of x and V can be obtained, however. The solution of the cubic equation leads to a result in the form of two slowly convergent infinite series.

A preferable procedure is to transform equation 2 into the dimensionless form

$$(\pi/6) (h/x)^3 + (\pi/2) (h/x) = V/x^3$$

and tabulate numerical solutions of h/x in terms of V/x^3 . Table 1 contains the values of h/x corresponding to values of V/x^3 from 0 to 2.0944, this being the range within which the angle remains acute.

TABLE 1
Related values of V/x^3 and h/x

V/x^3	h/x	V/x^3	h/x
0.0	0.0000	1.1	0.6206
0.1	0.0636	1.2	0.6656
0.2	0.1267	1.3	0.7089
0.3	0.1887	1.4	0.7504
0.4	0.2495	1.5	0.7904
0.5	0.3085	1.6	0.8288
0.6	0.3657	1.7	0.8659
0.7	0.4208	1.8	0.9016
0.8	0.4738	1.9	0.9361
0.9	0.5248	2.0	0.9695
1.0	0.5737	2.1	1.0018

TECHNIQUE

The solid to be investigated was imbedded on a paraffined glass plate. The liquid was placed in a short length of glass tubing, one end of which had been drawn out into a very fine capillary. A spiral in the capillary tube facilitated the manipulation of the tip. Drops of the liquid were formed slowly on the tip by gravitational force. By touching the glass tip to the solid surface at definite time intervals, drops of a constant and reproducible size were detached. Ten or more drops were measured at a time so that each determination yielded a truly average result. To minimize evaporation the solid and supporting plate were enclosed in a low form weighing bottle. The cover of this bottle was fitted with a window of optically plane glass. The diameters of the drops were observed through this window in the ocular scale of a low power microscope. The volume of liquid used for a given number of drops was obtained by measuring the difference in height of the liquid in the upper part of the glass tube before and after the drops were removed. Since the diameter of the tube was known, the cylindrical volume could be calculated.

In this investigation a tilting plate method and a direct observation method were used in order to check the measurements made by the spheroidal segment method. The procedure used in the tilting plate method was that of Adam and Jessop (1). In the visual observation method the apparatus was arranged so that the drop could be viewed directly in a

microscope. The eyepiece was fitted with an accurately centered cross-line micrometer disc and a pointer which indicated the angular measure on a scale fastened around the draw tube of the microscope. The glass tip on which the drop formed was allowed to remain on the surface under examination, so that expanding and contracting drops could be produced by changing the air pressure at the other end of the glass tube.

TABLE 2
Effect of drop size upon the contact angle
Distilled water on apple wax

RADIUS OF DROP	VOLUME OF DROP	CONTACT ANGLE CORRECTED
cm.	cm. ³	
0.1562	0.00365	58°
0.1212	0.00142	50°
0.0773	0.00039	53°
0.0687	0.00038	66°
0.0663	0.00041	74°
0.0601	0.00046	90°20'
0.0560	0.00035	88°30'
0.0418	0.00015	89°30'
0.0390	0.00012	88°50'

TABLE 3
Comparison of contact angles obtained by different methods

SYSTEM	METHOD	ANGLE OF CONTACT	
		Advancing	Receding
Distilled water on azobenzene.....	Spheroidal segment	89°	
	Tilting plate	90°	62°
	Direct observation	92°	64°
0.05 per cent soap solution on paraffin...	Spheroidal segment	48°	
	Tilting plate	48°	27°
	Direct observation	49°	30°
Distilled water on apple wax.....	Spheroidal segment	89°	
	Tilting plate	87°	62°

DISCUSSION OF RESULTS

Bartell and Hatch (2) found that a series of fairly large drops detached from a capillary tip formed widely different angles of contact on the same surface. This observation is confirmed by the results contained in the upper portion of table 2. But it is apparent that if the drop is made small enough, the angle attains a constant maximum value. In table 3 it is shown that this maximum is the advancing contact angle.

It has been shown (6, 9) that both expanding and contracting drops or bubbles may be caused to assume an equilibrium contact angle by tapping the support. This is true only for large drops, for vibration had no effect upon the advancing angles formed by small drops. Recent work has seemed to indicate that advancing and receding angles are themselves equilibrium angles for the surface under each of two different conditions (4).

From the foregoing it appears that the ease with which a drop may be made to spread further over a solid surface after having formed the advancing contact angle depends largely upon the drop size. The hydrostatic pressure due to the weight of the drop is exerted in the direction of further spreading. The capillary pressure within the drop is opposed to any extension of the liquid air surface. Since this pressure is inversely proportional to the radius of curvature, it will be greater in small drops. Hence with increasing drop size both the hydrostatic and capillary forces favor the probability of irregular extension of the drop.

CORRECTION FOR THE EFFECT OF GRAVITATIONAL FORCE ON THE FORM OF THE DROP

In the past considerable discredit has been cast upon sessile drop methods because unwarranted assumptions were made in the development of the mathematical equations to describe the form of the capillary surface. Therefore, in order that the proposed method may be employed with confidence, it is necessary to examine critically the effect of gravitational force upon the shape of the drop. The formulation of a correction term to compensate for this deviation from the spherical form would serve not only to evaluate the error due to this source, but also to determine the range of conditions within which the error is sufficiently small so that it may be ignored.

Consider a drop of liquid resting upon a solid surface OP under the influence of gravity and surface tension. In figure 1 the solid lines PR and PR' are the actual forms of two drops making contact angles of θ and θ' with OP . The dotted lines PQ and PQ' represent spherical surfaces and are the forms which the drops would assume if the gravitational force were removed. The surfaces PQ and PR have a common tangent PM , and PQ' and PR' also have a common tangent PM' .

The measured quantities are x and V , where V is the volume generated by rotating the area OPR about the OR axis. The equation for the contact angle requires that the volume be enclosed by a spherical surface. A spherical surface PQ' can be constructed such that the volume under PQ' is equal to that under PR (the true volume of the drop). This volume is used to calculate h , and the value of h/x thus obtained yields a value of $\theta'/2$ or θ' which is somewhat less than the true angle of contact θ .

By evaluating the small distance e , the true contact angle may be found from the equation

$$\tan (\theta/2) = (h + e)/x \quad (4)$$

In order to calculate e we need to have given the approximate angle of contact θ' , the radius x of the drop, and the capillary constant a of the liquid. From θ' and x the volume V' of the spherical segment POQ' may be calculated by geometrical methods. For the same angle θ' , the volume

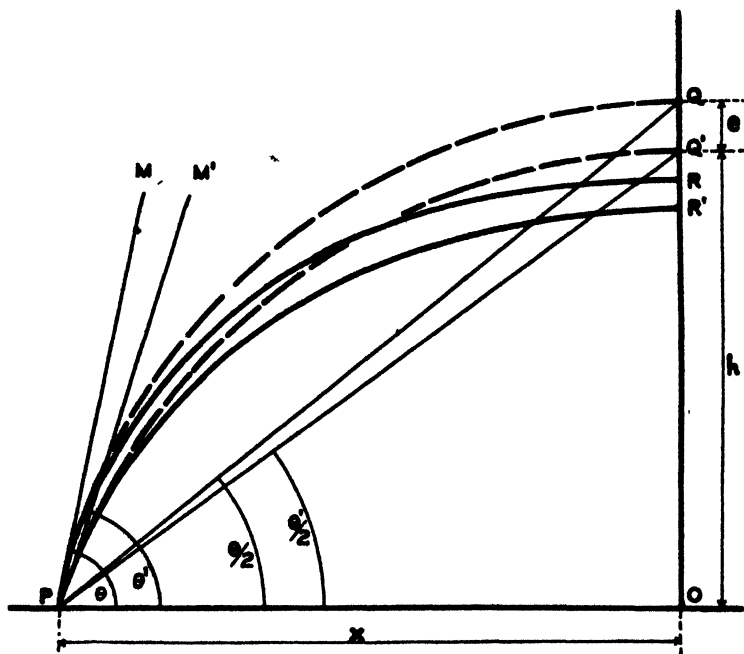


FIG. 1. Outline of a drop of liquid resting upon a solid surface under the influence of surface tension and gravity.

of the actual drop POR' may be calculated from the tables of Bashforth and Adams (5). Let the difference between the two volumes be $\Delta V' = V_{POQ'} - V_{POR'}$. If $(\theta - \theta')$ is small, $\Delta V'$ will be very nearly equal to $\Delta V = V_{POQ} - V_{POR}$. Since by construction $V_{POR} = V_{POQ'}$,

$$\begin{aligned} \Delta V &= V_{POQ} - V_{POQ'} \\ &= (\pi/6) [(h + e)^3 + 3x^2(h + e) - (h^3 + 3x^2h)] \end{aligned}$$

Since e is very small, the term e^3 may be ignored and the equation reduces to

$$e^2h + e(x^2 + h^2) - 2\Delta V/\pi = 0 \quad (5)$$

The general solution of the quadratic equation for e may be expressed in the form

$$e = -\left(\frac{x^2 + h^2}{2h}\right) \pm \left(\frac{x^2 + h^2}{2h}\right) \left[1 + \frac{8h\Delta V}{\pi(x^2 + h^2)^2}\right]^{1/2}$$

The terms within the brackets may be expanded in series according to the binomial theorem. After simplifying and expressing in numeric form, the equation becomes

$$\frac{e}{x} = \frac{2\Delta V/\pi x^3}{[1 + (h/x)^2]^{-1}} - \frac{(2\Delta V/\pi x^3)^2(h/x)}{[1 + (h/x)^2]^{-3}} + \frac{2(2\Delta V/\pi x^3)^3(h/x)^2}{[1 + (h/x)^2]^{-5}} - \dots \quad (6)$$

TABLE 4

Related values of θ' , x/a , and $\Delta V/x^3$

Values of $\Delta V/x^3$ are given in the body of the table for the corresponding values of θ' and x/a along the margins

θ'	x/a				
	0.1	0.2	0.3	0.4	0.5
90	0.017	0.041	0.085	0.143	0.208
85	0.011	0.029	0.062	0.105	0.154
80	0.008	0.021	0.046	0.078	0.115
75	0.006	0.016	0.034	0.059	0.088
70	0.004	0.012	0.026	0.045	0.068
65	0.003	0.009	0.020	0.035	0.053
60	0.003	0.007	0.016	0.027	0.041
50	0.002	0.005	0.010	0.017	0.026
40	0.001	0.003	0.006	0.011	0.016
30	0.000	0.002	0.004	0.007	0.011
20	0.000	0.001	0.002	0.004	0.006
10	0.000	0.000	0.001	0.002	0.003

Substituting this value of e/x in equation 4, one obtains

$$\tan(\theta/2) = \tan(\theta'/2) + (2\Delta V/\pi x^3) \cos^2(\theta'/2) - (2\Delta V/\pi x^3)^2 \tan(\theta'/2) \cos^6(\theta'/2) + \dots \quad (7)$$

The series is convergent if

$$[(8\Delta V/\pi x^3) \tan(\theta'/2) \cos^4(\theta'/2)]^2 < 1$$

It is apparent that no error need be involved in the previous assumption that $\Delta V' = \Delta V$, since a more exact value of ΔV may be obtained by successive approximations to the value of θ . Practically, the first approximation is well within the experimental error.

The relative magnitude of the correction terms in equation 7 may be

shown by means of an example. Suppose a drop of water to have the following characteristics: surface tension, 72.8 dynes per centimeter; radius, 0.1 cm.; contact angle, 90° . Then $V = 6.5 \times 10^{-5}$ cm.³, and the total correction due to the influence of gravity is $+1^\circ 10'$. In equation 7 the error in ignoring all correction terms beyond the first is $-0^\circ 0' 44''$. If the angle of contact is reduced to 60° , the radius and surface tension remaining the same, the total correction is only $+0^\circ 29'$. These calculations make it apparent that for the present purpose the gravitational effect is of little practical importance in measuring small contact angles.

CORRECTION FOR THE CURVATURE OF THE SOLID SURFACE

The application of the method can be extended to include solid surfaces with an approximately constant degree of curvature. Two corrections to the determined angle of contact must be made. First the tangent to

TABLE 5
Corrections for curvature of the solid surface
 $R/x = 20$

θ	ANGULAR CORRECTION $+2^\circ 52'$	
	Volume correction	Net correction
90	$-0^\circ 41'$	$+2^\circ 11'$
75	$-1^\circ 7'$	$+1^\circ 45'$
60	$-1^\circ 35'$	$+1^\circ 17'$
45	$-2^\circ 3'$	$+0^\circ 49'$
30	$-2^\circ 27'$	$+0^\circ 25'$
15	$-2^\circ 45'$	$+0^\circ 7'$
0	$-2^\circ 52'$	$+0^\circ 0'$

the solid surface at the point of contact is inclined at an angle to the horizontal plane through the base of the drop. This additive correction is partially counterbalanced by that due to the small solid segment which projects above the base of the drop.

If x is the radius of the drop, and R is the radius of curvature of the solid surface, the angular correction ϕ is given by the equation

$$\tan \phi/2 = R/x - \sqrt{(R/x)^2 - 1}$$

The change in contact angle caused by subtracting the volume of the solid segment from the volume of the drop may be calculated from ϕ and x according to the methods previously given (equations 1 and 3 and table 1). While the angular correction depends only upon R/x , the volume correction is also a function of the contact angle. Table 5 shows the relative values of these corrections when $R/x = 20$. The angular correction is almost exactly inversely proportional to R/x , and the volume correction

deviates only slightly more from the linear relationship. Hence for practical purposes, table 5 may be used for any value of R/x . It is only necessary to multiply any given correction by the appropriate value of $\frac{20}{R/x}$.

SUMMARY

A method has been devised for the determination of acute angles of contact which is largely independent of the form of the solid surface. It was shown that the contact angle is a function of the radius and volume of a small spherical drop of liquid.

An equation has been developed for evaluating the effect of gravitational force upon the form of the drop.

The validity of the method has been checked by repeating the determination of the contact angles upon the same materials by two different methods. Satisfactory agreement was obtained in all cases.

The author wishes to express his appreciation to Professor F. E. Bartell for much helpful advice.

REFERENCES

- (1) ADAM AND JESSOP: J. Chem. Soc. **127**, 1863 (1925).
- (2) BARTELL AND HATCH: Colloid Symposium Monograph **11**, 11 (1934).
- (3) BARTELL AND MERRILL: J. Phys. Chem. **36**, 1178 (1932).
- (4) BARTELL AND WOOLEY: J. Am. Chem. Soc. **55**, 3518 (1933).
- (5) BASHFORTH AND ADAMS: An Attempt to Test the Theory of Capillary Action. Cambridge (1883).
- (6) BOSANQUET AND HARTLEY: Phil. Mag. [6] **42**, 456 (1921).
- (7) O'KANE, WESTGATE, GLOVER, AND LOWRY: N. H. Agr. Expt. Station Tech. Bull. **39** (1930).
- (8) TAGGART, TAYLOR, AND INCE: Am. Inst. Mining Met. Engrs., Tech. Pub. **204** (1929).
- (9) WARK: J. Phys. Chem. **37**, 636 (1933).

THE DETERMINATION OF CONTACT ANGLES FROM MEASUREMENTS OF THE DIMENSIONS OF SMALL BUBBLES AND DROPS. II

THE SESSILE DROP METHOD FOR OBTUSE ANGLES¹

GUILFORD L. MACK AND DOROTHY A. LEE

*Division of Chemistry, New York State Agricultural Experiment Station,
Geneva, New York*

Received June 20, 1935

INTRODUCTION

It has been suggested in a previous communication (3) that widely variant surface energies may exist at closely adjoining points on a surface. Well-substantiated theory as to the surface structure of solid catalytic materials is in accord with this view (7). The "active patches" on the catalytic surfaces are an extreme example of irregularity in the surface energy, but it seems reasonable to suppose that such irregularities may exist to a lesser degree in nearly all ordinary surfaces. Photographic evidence in support of this proposition appears in the work of Wark and Cox (9), who found that the same air bubble under a mineral surface wet with water might have an angle of contact on the right side different from that on the left.

Instead of measuring the contact angle directly, it may be calculated from the dimensions of the drop. The angle so obtained may be regarded as the integral of the sum of all the various contact angles existing along the circumference of the drop. Thus each determination yields an average result not unduly influenced by irregularities at a given point on the surface.

For precise determinations the method should have an especial advantage over the usual procedure of direct measurement, because the error in personal judgment involved in drawing the tangent to the curved drop surface at the point of contact is eliminated. This error becomes increasingly important as the contact angle approaches 180°, while the dimensions of the drop may be measured with the same degree of accuracy as before.

If the image of the drop is recorded on a photographic plate, the capillary

¹ Presented at the Twelfth Colloid Symposium, held at Ithaca, New York, June 20-22, 1935.

Approved by the Director of the New York State Experiment Station for publication as Journal Paper No. 94, June 19, 1935.

constant of the liquid may be determined, without any additional experimental data, by the method of Dorsey (2). This serves as a valuable check upon the purity of the liquid-air interface and upon the reliability of the contact angle determination.

THEORETICAL

The tables of Bashforth and Adams (1) give the necessary information for calculating the contact angle from the dimensions of the drop. For the present purpose a considerable rearrangement of their data was necessary, because the units tabulated by them cannot be readily calculated from experimental data. In choosing other units, those have been selected which may be measured precisely or which may be readily calculated from other experimental data.

The most easily measured dimensions of the drop represented by figure 1 are the total height z and the radius r . These two lengths determine the

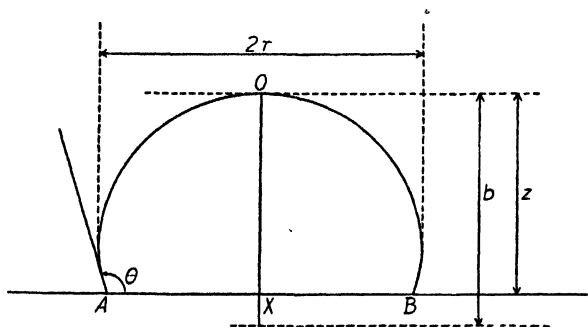


FIG. 1. Outline of a drop AOB resting upon the horizontal plate AB

size of the drop. Unfortunately, the contact angle depends not only upon the size of the drop but also upon its shape. In a drop of given size, the shape may be related to the capillary constant a of the liquid, or to the radius of curvature at the apex of the drop (b in figure 1). The contact angle is thus a function of two independent variables. Hence the contact angles contained in the body of table 1 must be related to both the size factor z/r listed in the vertical column at the left and to the shape factor r/b arranged in the horizontal column at the top of the table.

The procedure employed in making up table 1 was as follows: The original Bashforth and Adams tables contain, for each 5° interval of θ , values of z/b corresponding to given values of r/b and $\beta = 2b^3/a^2$. The values of z/r were found by dividing z/b by the corresponding value of r/b . Then for each value of θ , the values of z/r corresponding to equal increments of r/b were obtained by numerical interpolation. For each even value of r/b so obtained, the values of θ corresponding to equal incre-

ments of z/r were determined. This could be done with sufficient accuracy by means of graphical interpolation. The values of θ are correct to the nearest 0.1° . This error is well within the accuracy of most experimental data.

The calculations for the factor r/b have been extended only to $r/b = 0.90$. This is far enough to include a drop of water nearly 4 mm. in diameter.

TABLE 1
Values of θ corresponding to related values of z/r and r/b

$\frac{z}{r}$	$\frac{r}{b}$										
	1.00	0.99	0.98	0.97	0.96	0.95	0.94	0.93	0.92	0.91	0.90
0.90										90.6	91.5
0.95					90.1	90.9	91.8	92.7	93.7	94.6	95.6
1.00	90.0	90.8	91.7	92.5	93.5	94.4	95.4	96.4	97.5	98.7	99.8
1.05	92.9	93.8	94.8	95.7	96.8	97.9	99.1	100.4	101.6	102.9	104.2
1.10	95.7	96.8	97.9	99.1	100.3	101.6	102.9	104.3	105.7	107.3	108.8
1.15	98.6	99.9	101.1	102.4	103.9	105.3	106.8	108.5	110.1	111.9	113.7
1.20	101.5	102.9	104.3	105.9	107.5	109.1	110.9	112.8	114.7	116.8	118.9
1.25	104.5	106.0	107.6	109.4	111.2	113.1	115.1	117.3	119.6	122.0	124.6
1.30	107.5	109.2	111.0	113.0	115.1	117.3	119.7	122.2	124.9	127.8	131.0
1.35	110.5	112.5	114.6	116.8	119.2	121.8	124.6	127.6	130.8	134.3	138.3
1.40	113.6	115.8	118.2	120.8	123.5	126.5	129.9	133.5	137.6	142.0	147.3
1.45	116.7	119.3	122.1	125.1	128.3	131.8	135.8	140.3	145.5	152.1	161.4
1.50	120.0	123.0	126.1	129.8	133.4	137.7	142.8	148.9	157.1	173.3	
1.55	123.4	126.5	130.4	134.6	139.2	144.8	151.2	161.8			
1.60	126.9	130.8	135.1	140.1	146.1	153.8	167.0				
1.65	130.5	135.1	140.3	146.7	155.0	171.6					
1.70	134.4	139.8	146.4	155.1	174.2						
1.75	138.6	145.1	153.9	171.5							
1.80	143.1	151.4	165.9								
1.85	148.2	159.8									
1.90	154.2										
1.95	161.8										
2.00	180.0										

It has been shown (3) that greater precision in contact angle measurements can be attained by the use of small drops. Hence there is nothing to be gained by working with larger drops of correspondingly flatter shape.

The quantity b used in table 1 cannot be experimentally determined except by optical methods unsuited to the attainment of the requisite degree of accuracy. It may be readily calculated, however, from the value of the capillary constant a . The simplest relation between a and b is given by the equation

$$h = \frac{a^2}{b} \quad (1)$$

where h is the height of rise of the liquid in a capillary tube of unit radius. By substituting this value of h in Rayleigh's equation (4) for a in terms of r and h , and transforming, a solution for b is obtained in the form of an infinite series, as follows:

$$b = r + \frac{r^3}{3a^2} - \frac{2r^5}{9a^4} (3 \log 2 - 2) + \frac{r^7}{27a^6} (78 \log 2 - 53) - \dots \quad (2)$$

Verschaffelt (8) has developed equation 2 in this form as far as the third term on the right-hand side of the equation, and has pointed out its usefulness for calculating the value of b . By taking known values of b from the Bashforth and Adams tables, substituting the corresponding values of r and a in equation 2, and solving for b , the error involved by leaving off successive terms of the infinite series may be calculated. This procedure reveals an interesting fact which no one appears to have noticed heretofore. The last two terms in equation 2 add very little to the accuracy of the approximation even when r/a is small. For larger values of r/a , these latter terms actually increase the error beyond that existing after the calculation of the second term. The simplified equation

$$\frac{b}{r} = 1 + \frac{1}{3} \frac{r^2}{a^2} \quad (3)$$

is amply sufficient for the present purpose. For $r/a = 0.5$, the error in calculating b from equation 3 is 0.06 per cent, from equation 2 it is 0.05 per cent. These amounts are insignificant in comparison with the experimental error in determining the contact angle.

A further advantage in the use of equation 3 is that the value of a need be known only approximately. An error of 1 per cent in the determination of a produces an error of only 0.06 per cent in the value of b when $r/a = 0.3$. The value of r/a must be determined with great precision only when θ approaches 180° . For smaller angles, the values of r/a and r/b have much less effect on the determination of θ .

Sugden (6) has published a table which may also be used for finding r/b when r/a is known.

EXPERIMENTAL

The apparatus necessary to measure the dimensions of the small drops and bubbles consists of the following items. A low-power microscope is equipped with a filar micrometer eyepiece or a camera attachment. The solid surface requires a holder adjustable by rack and pinion movements in three directions. A microburet of the type used by Rehberg (5) is needed to form the very small bubbles and drops. The solid holder and the tip of the microburet project downward through the glass cover into an

absorption cell with plane glass sides. The cell holds the liquid into which air bubbles are blown, and, in the case of drops in air, it protects the surface from contamination by dust particles. Rapid evaporation of the very small drops is prevented by previously saturating the air within the cell

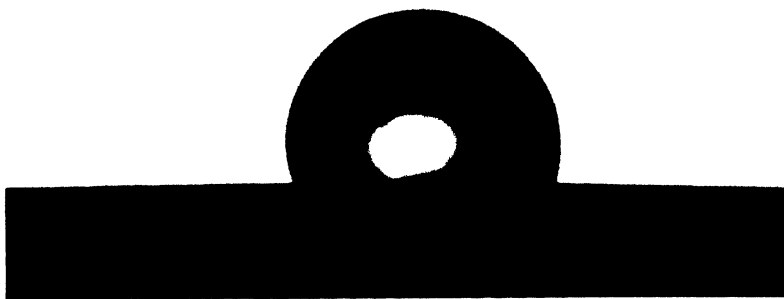


FIG. 2. Water drop on paraffin solidified in moist air. $z/r = 1.281$; $r/b = 0.9919$, θ (calculated) $= 107.7^\circ$; $\theta_l = 107.5^\circ$; $\theta_r = 102.8^\circ$.

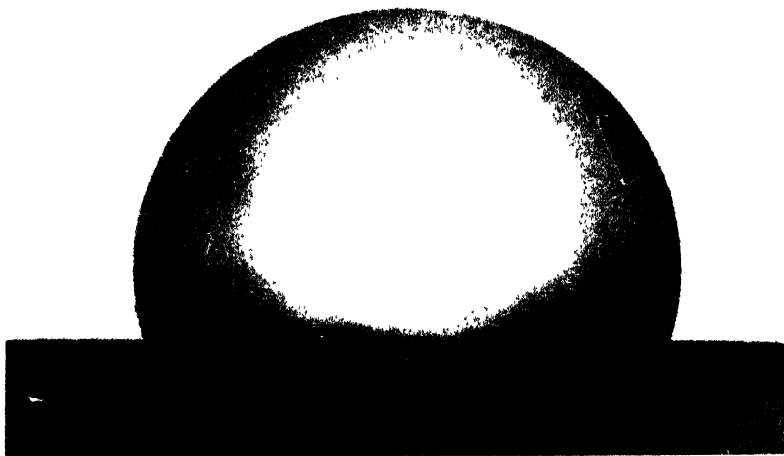


FIG. 3. Water drop on paraffin solidified in moist air. $z/r = 1.239$; $r/b = 0.9768$, θ (calculated) $= 107.4^\circ$; $\theta_l = 107.1^\circ$; $\theta_r = 107.3^\circ$.

with the vapor from other drops of the same liquid. A comparator or travelling microscope is convenient for measuring the small distances on the photographic plates, particularly if the capillary constant is to be determined by Dorsey's method (2).

The following cases will serve to illustrate the use of the proposed method of determining contact angles. The paraffin surfaces shown in figures 2 and 3 were solidified in air of 60 per cent humidity and then kept for one hour in the cell containing saturated water vapor. The drop in figure 2

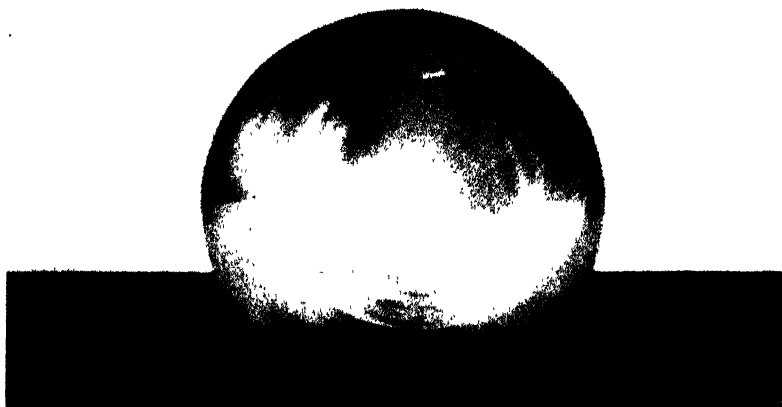


FIG. 4. Water drop on paraffin solidified in dry air. $z/r = 1.310$; $r/b = 0.9955$; θ (calculated) = 108.9° ; $\theta_l = 109.8^\circ$; $\theta_r = 108.0^\circ$.

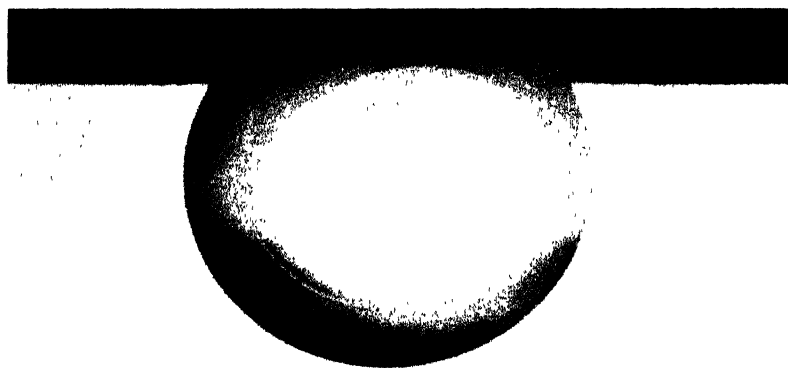


FIG. 5. Air bubble under paraffin immersed in 0.01 per cent soap solution. $z/r = 1.391$; $r/b = 0.9615$; θ (calculated) = $180 - 122.4 = 57.6^\circ$; $\theta_l = 57.8^\circ$; $\theta_r = 57.0^\circ$.

was selected as an extreme example of irregularity in a paraffin surface. It is apparent that the low value of the contact angle on the right side of the drop is not characteristic of the surface as a whole. The observed angle on the left side agrees well with the calculated value. Figure 3 shows

a much larger drop a little more than 2 mm. in diameter, while in figure 4 a fairly small drop of less than half that size is shown. In the latter case the paraffin was solidified in air dried over phosphorus pentoxide, and the photograph was taken immediately after the surface was placed in the absorption cell.

The method may be applied to bubbles as well as drops (figures 5 and 6). The paraffin surface is immersed in aqueous solutions of a proprietary spreading agent, and air bubbles are formed on the under side of the plate. The disadvantage of direct measurement is evident in figure 6. As the contact angle approaches 180° , it becomes increasingly difficult to draw the tangent to the curved surface at the point of contact. The dimensions z , r , and b may still be determined with the same degree of accuracy, however.



FIG. 6. An bubble under paraffin immersed in 0.1 per cent soap solution. $z/r = 1.659$; $r/b = 0.3936$; θ (calculated) = $180^\circ - 180^\circ = 0^\circ \pm 0.5^\circ$

SUMMARY

A method has been proposed for determining obtuse contact angles from measurements of three dimensions of sessile drops or bubbles under a plate. These dimensions are the vertical height z , the horizontal radius r , and the radius of curvature b at the apex of the curved surface.

A simplified equation is given for calculating the value of b from that of the capillary constant of the liquid.

The proposed method is shown to have several advantages over the direct method of measurement with a protractor.

REFERENCES

- (1) BASHFORTH AND ADAMS: An Attempt to Test the Theory of Capillary Action. Cambridge (1883)

- (2) DORSEY: J. Wash. Acad. Sci. **18**, 505 (1928).
- (3) MACK: J. Phys. Chem. **40**, 159 (1936).
- (4) RAYLEIGH: Proc. Roy. Soc. London **92A**, 184 (1915).
- (5) REHBERG: Biochem. J. **19**, 270 (1925).
- (6) SUGDEN: J. Chem. Soc. **119**, 1483 (1921).
- (7) TAYLOR: J. Phys. Chem. **30**, 145 (1926).
- (8) VERSCHAFFELT: Proc. Acad. Sci. Amsterdam **21**, 366 (1919).
- (9) WARK AND COX: Am. Inst. Mining Met. Engrs., Tech. Pub. No. 461.

ADSORPTION AT CRYSTAL-SOLUTION INTERFACES. IX

THE CONCENTRATION OF FOREIGN SUBSTANCES IN SOLUTION RELATIVE TO THE QUANTITY ADSORBED BY THE HOST CRYSTAL¹

WESLEY G. FRANCE AND PHOEBE P. DAVIS

Department of Chemistry, The Ohio State University, Columbus, Ohio

Received June 20, 1935

A number of explanations have been offered from time to time to account for the adsorption of impurities by crystals, but no satisfactory theory has yet been completely developed to account both for the selective nature of this adsorption and for the modifications of habit engendered in the host crystal by the impurity.

A review of the literature relevant to this problem reveals three general types of papers: (a) those attempting to find relationships between the amount of adsorbed material in the crystal and its concentration in the mother liquor (2, 3, 7, 8, 9, 10, 11, 20, 21, 22, 27, 28, 30, 34); (b) those attempting to account for the modifications of habit produced in crystals that are grown in the presence of impurities (1, 16, 18, 19, 24, 32); and (c) those presenting a general theory of the adsorption of impurities by growing crystals. The explanations offered by Buckley (4) and by France and coworkers (5, 12, 13, 14, 23, 25, 26, 29, 35) have been compared in an earlier paper (35). It has been suggested also that adsorption of impurities leading to habit modification is due to the same cause as oriented overgrowth (17). A close relationship between mixed crystal formation, adsorption of impurities by crystals, and oriented overgrowth has been found by Bunn (6) in the conditions necessary for their occurrence. He points out that mixed crystals and crystals built up by a continuous adsorption of impurity differ only in degree, and that the condition necessary for strong adsorption is similarity of lattice structure and interatomic dimensions in specific planes only of the two substances involved. This condition is the same that is known to be necessary for oriented overgrowth of different crystals on one another. Royer (31) has reached similar conclusions. In addition he finds (a) that the ions of the oriented crystal which replace those of the crystal support must have the same polarity as the latter, and (b) that the mode of linkage must be the same for replaced and replacing ions.

¹ Presented at the Twelfth Colloid Symposium, held at Ithaca, New York, June 20-22, 1935.

The development of a successful general theory has been impeded by two factors,—namely, the failure of workers to base conclusions of a theoretical nature on a sufficiently wide and diversified selection of data, and the absence of quantitative studies. The second of these factors is the more important, for until quantitative data have been assembled the laws governing the adsorption of impurities and the resultant habit modifications cannot be correctly known.

Therefore the chief purpose of this investigation was to determine quantitatively the relation between the concentration of impurity in solution and the amount of impurity adsorbed by a crystal grown spontaneously under equilibrium conditions. The substances selected for study were alkali halide crystals grown in the presence of urea as impurity, urea grown in the presence of alkali halides, and crystals of barium and lead nitrates and of ammonium and potassium alums grown in solutions containing various dyes. The halides ammonium chloride, sodium chloride, potassium chloride, and potassium bromide were chosen because their crystal structure is well known, and because urea greatly modifies the habit of sodium chloride and ammonium chloride and has very little effect on potassium chloride and potassium bromide. The nitrate and alum crystals were grown in the presence of dyes as a continuation of work on habit modification previously carried out in this laboratory.

Alkali halide crystals were grown from saturated salt solutions made up to contain a range of concentrations of urea. Crystallization took place at room temperature (23°C.) in 3-inch crystallizing dishes provided with paper covers to keep out dust and air currents. The crystals were removed for analysis after approximately 5 per cent of the salt had crystallized out. They were washed once with water and dried at room temperature. The same procedure was followed with urea crystals grown in the presence of alkali halides and with nitrate and alum crystals obtained from solutions containing dye. Thirty-one sets of crystals were grown and analyzed, each involving on an average ten concentrations of impurity. In some cases several sets of crystals were grown and analyzed for the same pair of substances.

The number of moles of adsorbed impurity per mole of host crystal were determined in both the solution and solid phases for all crystallizations made. The crystals containing adsorbed dye were analyzed for dye content, using a Duboscq type of colorimeter. Analysis for halide present in urea crystals and in the ammonium chloride crystals contaminated with urea was made by titration with silver nitrate, using a dichromate indicator. The other alkali halide crystals containing urea were analyzed for urea content by a gas analysis method involving the reaction between urea and alkaline sodium hypobromite to produce nitrogen.

An ultramicroscopic examination was made of two solutions containing

dyes, to observe any possible relation between the concentration of colloidal particles in the solution and the amount of dye taken up. X-ray powder spectrographs were made in several cases, in order to discover any change in lattice constants produced by the impurity. Optical examinations with a polarizing microscope were made of a number of crystals to observe the presence or absence of dichroism.

The data obtained disclose the following facts about the nature of the adsorption process.

(1) A plot of the number of colloidal particles observed ultramicroscopically against the concentration of dye in the solutions studied shows that a linear relation exists between the two quantities. On the other hand, the amount of dye taken up by the crystals obtained from these

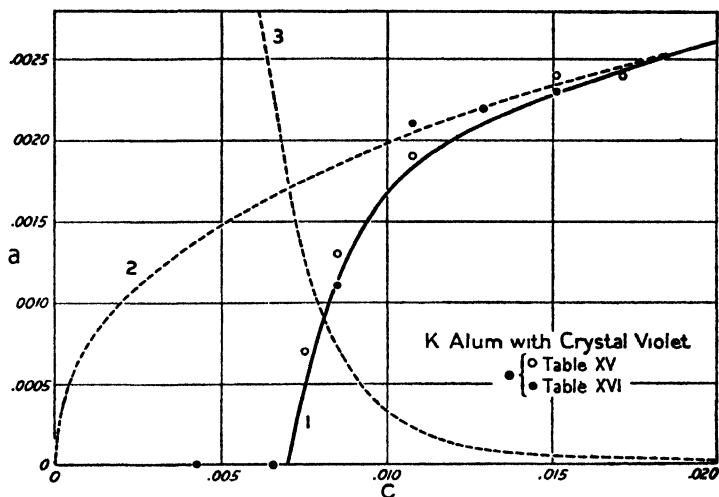


FIG. 1

solutions plotted against the dye concentration follows a type of exponential curve which starts at a considerable distance from the origin (cf. curve 1, figure 1). It must therefore be concluded that in the crystals studied the amount of dye taken up is not related to the number of colloidal particles present in the dye-salt solutions. These results are in agreement with those obtained by one of us in earlier studies of a somewhat similar nature (14).

(2) A careful checking of four x-ray powder spectrographs for the four pairs of substances (1) pure sodium chloride-sodium chloride + urea, (2) pure sodium chloride-sodium chloride + chromic chloride, (3) pure urea-urea + sodium chloride and (4) pure lead nitrate-lead nitrate + methylene blue showed that in all cases there was no displacement of the

lines produced by the contaminated crystals, and therefore no appreciable change in the lattice constant due to the adsorption of impurities. This interesting result is in agreement with work reported by earlier investigators (13, 33). The absence of lattice distortion may be due to (a) the presence of too little impurity to produce a perceptible distortion, (b) some type of interstitial adsorption such that the host crystal envelopes the molecules of impurity without alteration of its space lattice, or (c) similarity of the lattice constants in one plane of the host crystal to those in one plane of the foreign crystal so that deposition occurs in such a way that the similar planes coincide.

(3) Pronounced dichroism was observed in thirty-one out of thirty-two crystals of ammonium alum colored with Pontamine Sky Blue 6B, and a characteristic but less pronounced dichroism was shown by ammonium alum crystals colored with crystal violet. This dichroism may be accounted for by the assumption that the dye molecules are oriented with respect to themselves and to the face on which they are adsorbed. The color effects observed under the polarizing microscope lead to the view that the dye molecules were probably adsorbed with their long axes perpendicular to the cube faces of the alum crystals. Neither potassium nor ammonium alum crystals colored with dye No. 11 showed dichroism; several types of random distribution of dye molecules might lead to this absence of dichroism.

(4) Points shown in figures 1, 2, and 3 show typical results obtained when a , the concentration of foreign material deposited in the crystals expressed as moles of foreign material per mole of host crystal, is plotted against c , the number of moles of impurity per mole of crystal in the solution. The curves obtained in similar plots of thirty-one sets of crystallizations were tested to determine whether or not they were described by the more common adsorption equations, including the adsorption isotherm and Langmuir's equation for monomolecular adsorption of gases.

Figure 4, constructed from the same data as that in figure 1, shows that a curve is obtained instead of a straight line as required by the logarithmic form of the equation of the adsorption isotherm. Likewise a curve results (figure 5) instead of a straight line when the c/a and c values, obtained from a rearrangement of the Langmuir equation in which the concentration c is substituted for the pressure p , are plotted against each other. From figures 4 and 5 it would seem that something more than a simple adsorption process describable by either the adsorption isotherm or the Langmuir equation is involved when a dye is taken up from a solution by a growing salt crystal. Freundlich (15) has shown that the retardation of crystallization by varying quantities of foreign substances is expressed by an exponential of the same form as the adsorption isotherm. This would indicate that an adsorbed layer of impurity expressed by the adsorption

isotherm is formed at the surface of a growing crystal. It is evident from the failure of the curves obtained in this study to pass through the origin (cf. figures 1 and 2 as typical examples) that either some condition exists or a process occurs during crystal growth which prevents, at least at low dye

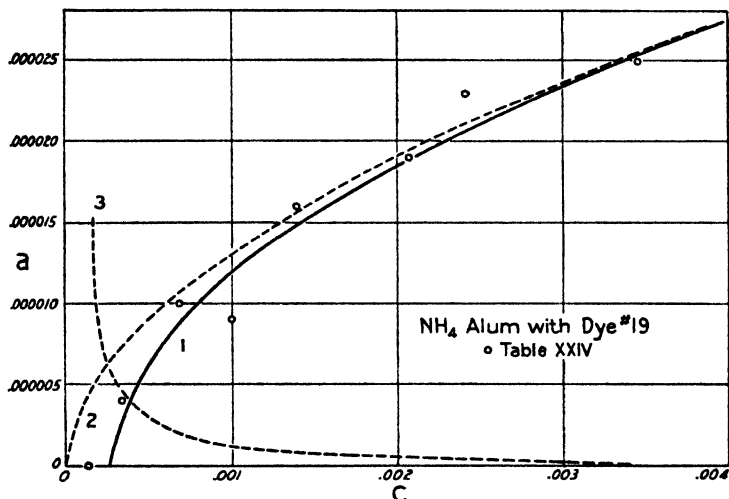


FIG. 2

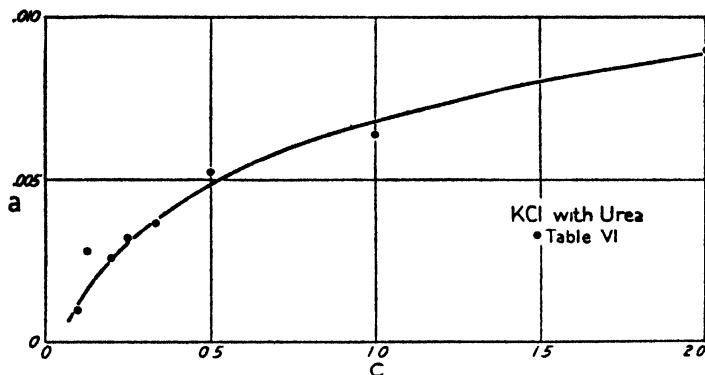


FIG. 3

concentrations, the incorporation of the expected amount of dye in the growing crystal.

An attempt was therefore made to find an empirical equation relating a and c , which would take into account this counter-adsorption process. It was assumed, partly from the appearance of the a - c curves (curves No. 1 in figures 1 and 2) and partly from the tendency of the $\log a$ - $\log c$ curves (figure 4) to become linear at high values of c and a , that the counter-

adsorption process is significant only at low values. Values of k and $1/n$ were then found for the adsorption curve which reproduced the best smooth curve through the experimental points at higher concentrations. The lower part of the curve was then found to be obtainable by assuming that

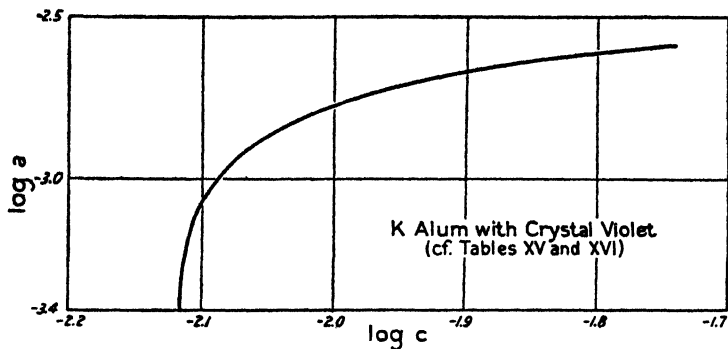


FIG. 4

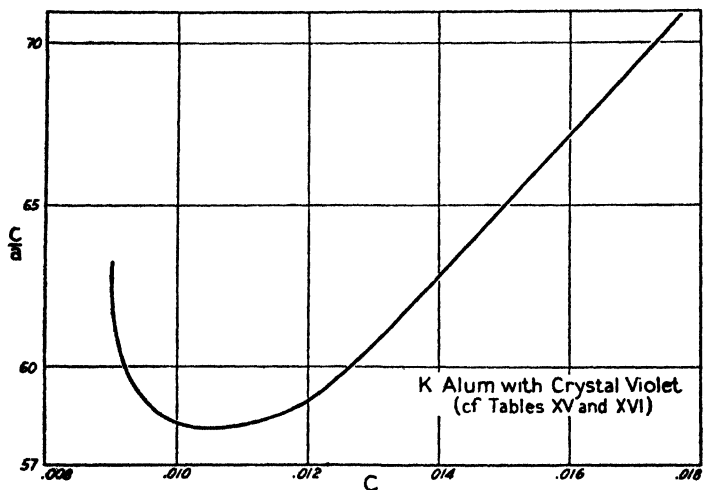


FIG. 5

the counter-adsorption process was represented by an expression of the form

$$a' = k'c^{-1/n'} \quad (1)$$

and that the experimental curve was the difference between an adsorption isotherm and this second exponential. Thus the experimental data are expressed fairly well in all cases by the relation

$$a = kc^{1/n} - k'c^{-1/n'} \quad (2)$$

The significance of the second term in the right-hand member of the equation is not completely evident; but it seems to indicate that whatever the nature of the counter-adsorption process, it is a function, primarily, of the dye concentration, is infinite at zero dye concentration, and rapidly approaches zero even at low concentrations. This conclusion, together with the results obtained in earlier work of the authors on the effect of stirring and growth ratios on the habit and dye adsorption of alum crystals (29), suggests the following explanation for the failure of the curves to pass through the origin. Those faces of a normally growing crystal having the stronger fields of force are the ones that experience the most rapid perpendicular displacement. As a result of this rapid growth there is a tendency to lower the concentration of the crystal ions in the layer of solution adjacent to the rapidly growing faces. Any effect acting to maintain a higher concentration of the crystal ions in this layer should result in an accelerated displacement of these faces. Thus in the case of potassium alum the growth ratio (100)/(111) was increased from 1.61 to 1.75 by rapid stirring. It would seem therefore that in the presence of an adsorbable dye the crystal takes up its own ions in preference to the dye as long as such ions are readily available. However, in the absence of a plentiful supply of its own ions the crystal will satisfy its growth forces by taking up adsorbable dye ions or molecules when the concentration of the dye adjacent to the rapidly growing face becomes sufficiently great relative to that of the crystal ions. The distance from the origin to the point of intersection of the curve with the c axis apparently represents the minimum dye concentration required to establish this condition.

In figures 1 and 2, curve 1 represents the values of a calculated from equation 2, curve 2 values from the equation of the adsorption isotherm, and curve 3 those from equation 1. It should be noted that equation 2 predicts that at high values of c the adsorption isotherm would fit the data; this was not always found to be true because of the precipitation of part of the dye at higher concentrations in some instances.

In the case of the systems alkali halides-urea it was not possible to obtain even approximately accurate values of the amount of foreign material adsorbed at low concentrations, and hence to extend the curve to zero adsorption and also to fit equation 2 unequivocally. Qualitatively, however, it is evident that the adsorption curves are similar to those for dyes adsorbed by salts (cf. figure 3), and it seems quite likely that equation 2 would fit if sufficient data were available at low concentrations of impurity to warrant its application.

One fact of interest with regard to the adsorption of urea by the alkali halides studied should be noted. In spite of the fact that ammonium chloride and sodium chloride crystals are much more modified in habit by the presence of urea, potassium chloride and potassium bromide crystals adsorb a larger quantity of this impurity.

SUMMARY

1. No relation was found between the number of colloidal particles of dye present in solution, and the amount of dye adsorbed by a given host crystal.

2. X-ray powder spectrographs of crystals containing adsorbed impurities showed the same lattice constants for impure as for pure crystals.

3. The dichroism observed in crystals containing adsorbed dye is accounted for by the assumption that the dye molecules are oriented with respect to themselves and to the face on which they are adsorbed. The color effects observed under the polarizing microscope in crystals of ammonium alum and dye No. 13 lead to the view that the dye molecules are adsorbed with their long axes perpendicular to the cube faces of the alum crystal.

4. The data for the adsorption of dye by alum and nitrate crystals failed to fit either the Langmuir or the adsorption isotherm equation, but were reproduced over most of the range by the equation

$$a = kc^{1/n} - k'c^{-1/n'}$$

5. The second term in the right-hand member of equation 2 indicates the occurrence of a counter-adsorption process. Examination of this term shows (a) that adsorption does not commence at $c = 0$ but at a value of c such that

$$kc^{1/n} = k'c^{-1/n'}$$

and (b) that $k'c^{-1/n'}$ possesses the value ∞ at $c = 0$ but falls off rapidly to zero at low values of c .

6. Equation 2 predicts that at high values of c an adsorption isotherm would fit the data within the limits of error, but this was not always found to be true because of the precipitation of part of the dye at higher concentrations.

REFERENCES

- (1) BALAREFF: *Kolloid-Beihefte* **30**, 249 (1930); **32**, 304; **33**, 279 (1931); **34**, 441 (1932); **37**, 180, 324 (1933).
- (2) BALCAR AND STEGEMAN: *J. Phys. Chem.* **32**, 1411 (1928).
- (3) DE BROUCKÈRE: Thesis, University of Brussels, 1932.
- (4) BUCKLEY: *Z. Krist.* **73**, 443; **75**, 15; **76**, 147; **78**, 412 (1930); **80**, 238 (1931); **81**, 157; **82**, 37 (1932); **85**, 58 (1933); **88**, 122, 181, 248 (1934).
- (5) BENNETT AND FRANCE: *J. Am. Ceram. Soc.* **11**, 571 (1928).
- (6) BUNN: *Proc. Roy. Soc. London* **141A**, 567 (1933).
- (7) CHLOPIN: *Z. anorg. Chem.* **143**, 97 (1925); *Ber.* **64**, 2635 (1931).
- (8) CHLOPIN AND NITIKIN: *Z. anorg. Chem.* **166**, 311 (1927).
- (9) CHLOPIN AND POLESSITZKY: *Z. anorg. Chem.* **172**, 310 (1928).
- (10) CHLOPIN, POLESSITZKY, AND TOLMATSCHOFF: *Z. physik. Chem.* **145A**, 57 (1929).
- (11) DOERNER AND HOPKINS: *J. Am. Chem. Soc.* **47**, 662 (1925).

- (12) ECKERT AND FRANCE: J. Am. Ceram. Soc. **10**, 579 (1927).
- (13) FOOTE, BLAKE, AND FRANCE: J. Phys. Chem. **34**, 2236 (1930).
- (14) FRANCE: Colloid Symposium Monograph **7**, 59 (1930).
- (15) FREUNDLICH: Z. physik. Chem. **75**, 245 (1910).
- (16) FRONDEL: Am. Mineral. **19**, 316 (1934); Am. Museum Novitates 695, 758, 759 (1934).
- (17) GAUBERT: Compt. rend. **180**, 378 (1935).
- (18) GRIMM: Z. physik. Chem. **98**, 353 (1921); Z. Elektrochem. **28**, 75 (1922); **30**, 467 (1924); Z. Krist. **57**, 574 (1922); Handbuch der Physik **24**, 581 (1927).
- (19) GRIMM AND WAGNER: Z. physik. Chem. **132**, 131 (1928).
- (20) HAHN, KADING, AND MUMBRAUER: Z. Krist. **81**, 387 (1934).
- (21) HENDERSON AND KRACEK: J. Am. Chem. Soc. **49**, 738 (1927).
- (22) KAMMER AND SILVERMAN: J. Am. Chem. Soc. **47**, 2514 (1925).
- (23) KEENEN AND FRANCE: J. Am. Ceram. Soc. **10**, 821 (1927).
- (24) KOLTHOFF: J. Phys. Chem. **36**, 860 (1932).
- (25) LASH AND FRANCE: J. Phys. Chem. **34**, 724 (1930).
- (26) MCBURNEY AND FRANCE: J. Am. Chem. Soc. **46**, 540 (1924).
- (27) MARC: Z. physik. Chem. **75**, 710 (1911).
- (28) MUMBRAUER: Z. physik. Chem. **156A**, 113 (1931).
- (29) PAINE AND FRANCE: J. Phys. Chem. **39**, 425 (1935).
- (30) POLESSITZKY: Z. physik. Chem. **161A**, 325 (1932); **167A**, 349 (1934).
- (31) ROYER: Bull. soc. franç. minéral. **51**, 7 (1928); Compt. rend. **198**, 185, 585, 949, 1868 (1934).
- (32) SMEKAL: Z. angew. Chem. **42**, 489 (1929).
- (33) SWARYCZWESKI: Bull. intern. acad. polonaise **1932A**, 128; Chem. Abstracts **27**, 3866 (1933).
- (34) WALTER AND SCHLUNDT: J. Am. Chem. Soc. **50**, 3266 (1928).
- (35) WEINLAND AND FRANCE: J. Phys. Chem. **36**, 2832 (1932).

SPECTROSCOPIC ESTIMATION OF ADSORBED IONS¹

MAY ANNETTS AND LORNE NEWMAN

McLennan Laboratory, University of Toronto, Toronto, Canada

Received June 20, 1935

Theories of colloid stability, of the mechanism of coagulation, and of the charge on the colloid particle are all intimately related to the adsorption of ions. A knowledge of the total number and kinds of ions adsorbed by colloidal particles under given conditions would greatly assist in the understanding of colloidal behavior.

Attempts have been made to measure such adsorption by chemical analysis (12, 11, 2), but the concentrations to be measured are so small (usually from $0.0001M$ to $0.00001M$) that ordinary chemical methods are not sufficiently sensitive.

Concentration cells have been used to measure the number of ions remaining free in the intermicellar liquid after adsorption has taken place (4, 10). The field of application of this method is very limited, and furthermore many difficulties, such as the effects due to the activity of the ions and the presence of foreign substances, are encountered in the interpretation of these results.

Quantitative spectrum analysis for the measurement of small quantities of materials has been developed rapidly during the past few years. This paper applies emission spectrum analysis to the estimation of the adsorption of ions in colloidal solutions.

The spectra may be excited in various ways; the methods used with solutions are outlined below: (1) The flame method of Lundgårdh (7, 9, 6) is the most sensitive one for use with the alkali metals. The solution to be investigated is vaporized and mixed with the illuminating gases in a special burner. Using 2 or 3 cc. of solution the probable error is claimed to be as low as 2 to 5 per cent. (2) The uncondensed spark method is the one recommended by Gerlach (5) for general work. A high voltage spark takes place between the surface of the solution and a metal electrode suspended above it. So much heat is produced by the spark that it is necessary to cool the electrode by surrounding it with ice or cold water (see figure 1). (3) Recently Gerlach (5) used an interrupted arc with the same types of electrodes as described in the second method. The arc

¹ Presented at the Twelfth Colloid Symposium, held at Ithaca, New York, June 20-22, 1935.

between the surface of the liquid and the metal electrode is opened and closed several times a second by a cam arrangement run by an electric motor. This method is particularly useful in cases where it is desirable to reduce the intensity of unavoidable band spectra. (4) Twyman and Hitchen (8), and Brode and Steed (1) use a spark between two liquid jets in order to avoid contamination at the sparking surfaces.

In this work the uncondensed spark method was used in conjunction with a Hilger medium quartz spectrograph E2. Sensitive plates giving good contrast are required; Ilford's Zenith and Hypersensitive Panchromatic plates were used. By suitably adjusting a spherical condensing

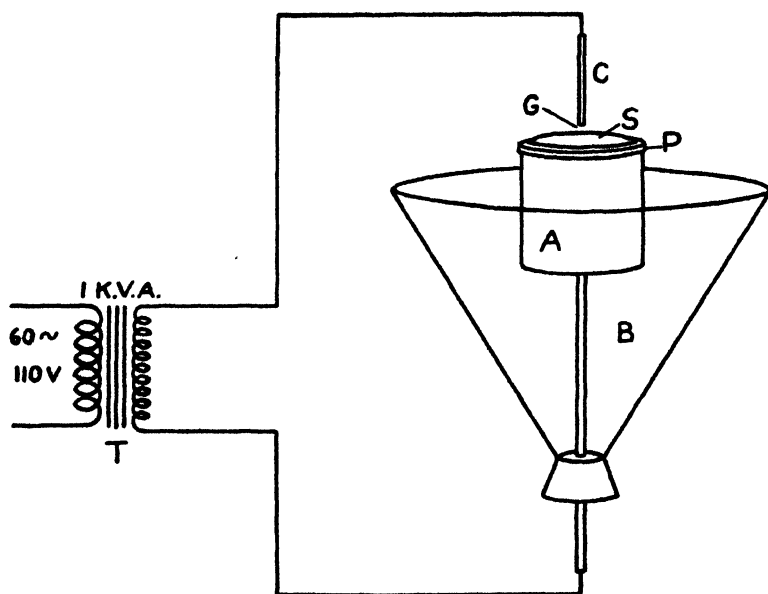


FIG. 1. The apparatus. A, iron block; B, ice; C, copper electrode; G, gap ca. $3/8''$; P, platinum cap; S, solution, 5 cc.

lens the intensity of the spectrum due to the metal electrode may be greatly reduced and that due to the substances in solution increased, since the points of maximum emission of the two spectra are some distance apart.

The gold colloid used in this investigation was prepared by under-water sparking at a voltage of about 10,000 and a frequency of about 10^6 cycles per second. In the first experiments the usual salts were used,—sodium hydroxide as stabilizer (added to the water before sparking) and aluminum chloride as coagulating electrolyte. As the spectroscopic method of analysis is only suitable for use with metal ions, later experiments were confined to the use of salts containing metals in both ions,—sodium

permanganate as stabilizer and magnesium chromate as coagulating electrolyte.

The amount of electrolyte *necessary* to coagulate the sol was taken as the *minimum* quantity which when mixed with an equal volume of the sol caused complete precipitation of the colloidal material in about three days.

For analysis the coagulated solution was first centrifuged to obtain good separation of the precipitated gold and the supernatant liquid. This liquid was poured off and the gold was dissolved in aqua regia and diluted to the same volume as the supernatant liquid. When testing for aluminum it was necessary to concentrate the solutions to one-fiftieth of their original volume to get measurable concentrations; when testing for magnesium it was not necessary to concentrate at all. All solutions were made slightly acid before analysis, as this has been found to increase greatly the spectroscopic sensitivity.

Plates were also taken with gold sols precipitated by freezing in liquid air, i.e., without the addition of any coagulating electrolyte; and with copper sols prepared as the gold sols were but without the addition of any stabilizing electrolyte, and precipitated by magnesium chromate.

The concentrations of metal ions in the unknown solutions were found by comparing the intensities of certain lines in their spectra with the intensities of those lines in the spectra of standard solutions which were taken on the same plate under the same conditions of excitation, exposure, etc. The intensities were compared visually, as it was found that with practice this method was just as satisfactory as using a microphotometer. The uniformity of lines due to some reference material present in all the solutions in equal concentration is usually considered as proof that electrical conditions have remained the same throughout a series of exposures.

In general the probable error was about 10 per cent of the amount measured. (In spectrum analysis the error is a certain percentage of the amount present and not an absolute amount, as in most chemical methods.) When the distribution of an ion between the supernatant liquid and the precipitate is very unequal, say ten to one, the amount of the ion adsorbed may be determined with much greater accuracy—often to within 1 or 2 per cent of the amount added—for the error involved is 10 per cent of the smaller amount analyzed. In all spectrum analysis work the sensitivity varies considerably with the element investigated, with the type of spectrograph, with the type of photographic plate, with the conditions of excitation, the length of exposure, etc. In this investigation the following limits of sensitivity have been found: $M/100,000$ for gold, manganese; $M/50,000$ for magnesium, chromium, sodium; $M/1,000$ for aluminum. Some elements, for example, sodium, are often present in the purest materials obtainable, or in the air, in concentrations sufficient to be visible spectroscopically. Such concentrations can be allowed for by including a suitable blank spectrum on each test plate.

The results up to the present may be summarized as follows:

I. See figure 2A. The sodium lines are clearly visible in the photograph with the supernatant liquid (No. 7), and cannot be seen at all with the precipitated gold (No. 2). The aluminum lines appear with the gold (No. 2) and cannot be seen with the supernatant liquid (No. 7).

FIG. 2. Spectra showing metal lines in the coagulating liquids taken in various strengths as standards and for comparison lines present in spectra of supernatant liquid and coagulated material. Details of individual spectra are given below.

A. Gold sol, 0.8 g. per liter (stabilized by 0.001 *M* sodium hydroxide)

1. Aluminum chloride solution in concentration just sufficient to produce coagulation—*M*/10,000.
2. Gold precipitated by 1 and dissolved in acid.
3. Aluminum chloride solution, 80 per cent of the strength of 1.
4. Aluminum chloride solution, 60 per cent of the strength of 1.
5. Aluminum chloride solution, 40 per cent of the strength of 1.
6. Aluminum chloride solution, 20 per cent of the strength of 1.
7. Supernatant liquid corresponding to 2.
8. Acid blank.

B. Gold sol, 0.8 g. per liter (stabilized by 0.001 *M* sodium permanganate)

1. Supernatant liquid from gold sol precipitated by freezing in liquid air.
2. *M*/1000 sodium permanganate solution.
3. *M*/5000 sodium permanganate solution.
4. *M*/25,000 sodium permanganate solution.
5. *M*/125,000 sodium permanganate solution.
6. Precipitated gold corresponding to 1.
7. Acid blank.

C. Gold sol, 0.8 g. per liter (stabilized by 0.001 *M* sodium permanganate)

1. 0.00040*M* magnesium chromate and *M*/10,000 sodium permanganate.
2. 0.00035*M* magnesium chromate and *M*/10,000 sodium permanganate.
3. 0.00030*M* magnesium chromate and *M*/10,000 sodium permanganate.
4. 0.00025*M* magnesium chromate and *M*/10,000 sodium permanganate.
5. Gold precipitated by *M*/8000 magnesium chromate and dissolved in acid.
6. Gold precipitated by *M*/12,000 magnesium chromate and dissolved in acid (minimum amount necessary for coagulation).
7. Supernatant liquid corresponding to 5.
8. Supernatant liquid corresponding to 6.
9. 0.00020*M* magnesium chromate and *M*/10,000 sodium permanganate.
10. 0.00015*M* magnesium chromate and *M*/10,000 sodium permanganate.
11. 0.00010*M* magnesium chromate and *M*/10,000 sodium permanganate.
12. 0.000066*M* magnesium chromate and *M*/10,000 sodium permanganate.
13. Acid blank.

D. Copper sol, 0.6 g. per liter

1. Copper precipitated by *M*/25,000 magnesium chromate and dissolved in acid (minimum amount necessary for coagulation).
2. Supernatant liquid corresponding to 1.
3. Acid blank.

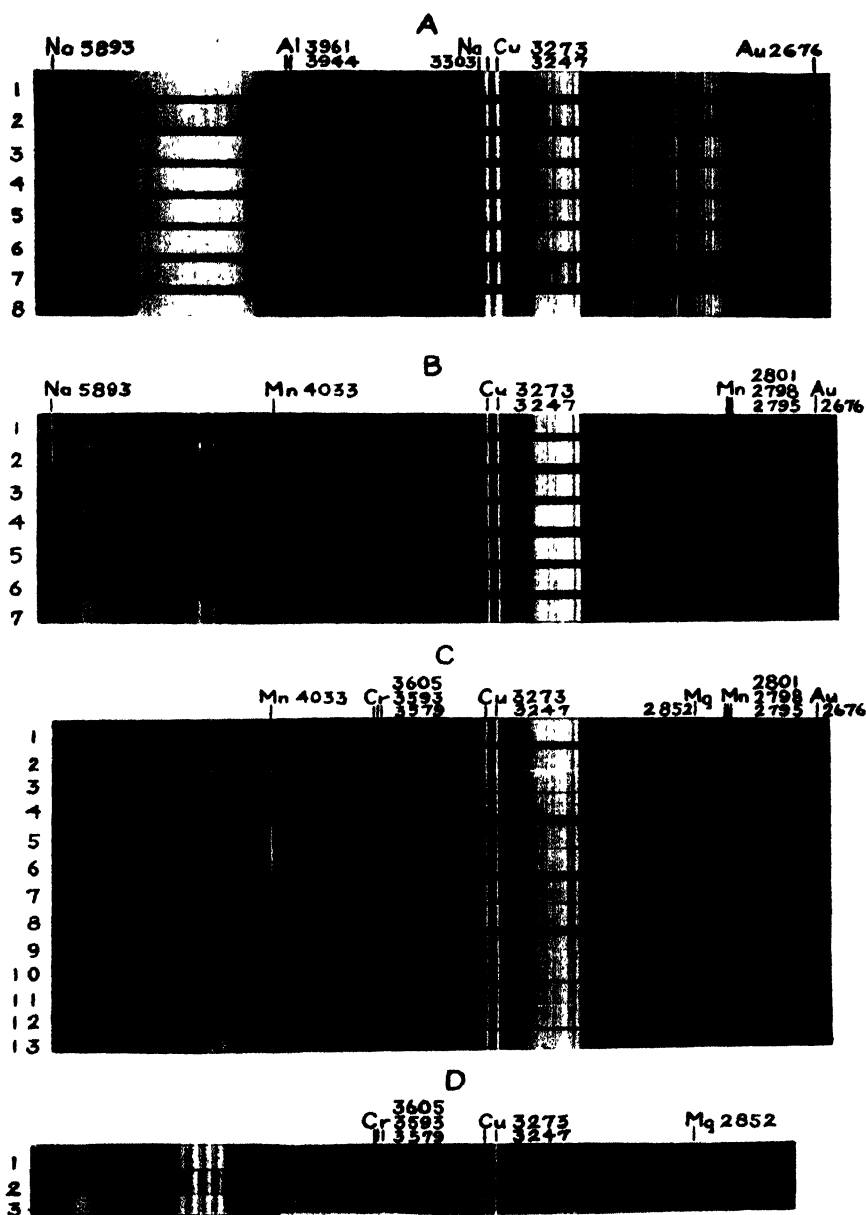


FIG. 2

Thus when gold sols stabilized by sodium hydroxide are precipitated by aluminum chloride, at least 90 per cent of the aluminum ions are adsorbed by the gold and at least 98 per cent of the sodium ions remain in the supernatant liquid. The gold particles acquire a negative charge in preparation, presumably by the adsorption of hydroxyl ions. Owing to this negative charge the gold attracts the trivalent positive ion of the coagulating electrolyte, but leaves the monovalent positive ion of the stabilizing electrolyte free in the supernatant liquid.

II. See figure 2B. The manganese lines are very prominent in the photograph with the precipitated gold (No. 6), but are not visible at all with the supernatant liquid (No. 1). The sodium line is visible in all the spectra but its concentration in the precipitated gold (No. 6) is no higher than that in the acid blank (No. 7).

When gold sols stabilized by sodium permanganate are precipitated by freezing in liquid air, at least 99 per cent of the manganate ions are precipitated with the gold and 95 to 98 per cent of the sodium ions remain free in the supernatant liquid. This is not in agreement with the theory of those who believe that the non-stabilizing ion of the stabilizing electrolyte (the sodium in this case) appears free in the supernatant liquid only when displaced from the neighborhood of the particles by the coagulating electrolyte.

III. See figure 2C. Chromium lines are visible in No. 7 and No. 8—the supernatant liquid—but not in No. 5 and No. 6—the precipitated gold. The magnesium line is much more intense in No. 7 and No. 8—the supernatant liquid—than in No. 5 and No. 6—the precipitated gold. The manganese lines may be clearly seen with the gold as in figure 2B; not a trace of them appears with the supernatant liquid.

When gold sols stabilized by sodium permanganate are precipitated by magnesium chromate, at least 95 per cent of the chromium ions remain in the supernatant liquid. Chromium cannot be detected with the precipitated gold until about twenty times the minimum coagulating concentration of magnesium chromate is added to the colloid.

When just sufficient magnesium chromate is added to produce coagulation, about one-third of the magnesium ions is adsorbed by the gold. The amount of magnesium adsorbed increases slightly (about three times) when many times (up to eighty times) this amount of magnesium chromate is added. At least part of this increase is due to traces of supernatant liquid remaining with the precipitated gold. The precipitate was not washed, as it was found difficult to be certain that washing the precipitate did not remove some of the adsorbed ions (see also Weiser (10)).

These results are not in agreement with those of Freundlich (4) or of Euler and Zimmerlund (3). Freundlich found that appreciable amounts of both ions of the coagulating electrolyte were adsorbed by the precipi-

tated particles of an "electrolyte-free" gold sol. Euler and Zimmerlund found that equal amounts of both ions of an electrolyte were adsorbed by fine gold powder.

IV. See figure 2D. Here the chromium lines may be clearly seen in No. 1, the precipitated copper, but not at all in the supernatant liquid (No. 2); while the magnesium line appears strongly in No. 2 but not at all in No. 1.

Thus when copper sols, which are positively charged, are precipitated by the minimum necessary quantity of magnesium chromate, at least 90 per cent of the chromate ions are adsorbed by the copper and at least 95 per cent of the magnesium ions remain in the supernatant liquid. This distribution is, of course, just opposite to that obtained in a negatively charged gold sol; there the magnesium ions are adsorbed and the chromium ions left in the supernatant liquid.

Further work is now in progress.¹

In conclusion, the authors wish to express their sincere appreciation to Professor E. F. Burton, Director of the McLennan Laboratory at the University of Toronto, for his suggestion of the problem and his advice throughout the investigation.

REFERENCES

- (1) BRODE AND STEED: *Ind. Eng. Chem., Anal. Ed.* **6**, 157 (1934).
- (2) CHAKROVARTI, GHOSH, AND DHAR: *J. Phys. Chem.* **34**, 326 (1930).
- (3) EULER AND ZIMMERLUND: *Arkiv. Kemi Mineral. Geol.* **8**, No. 14 (1921-23).
- (4) FREUNDLICH, JOACHIMSOHN, AND ETTISCH: *Z. physik. Chem.* **141A**, 249 (1929).
- (5) GERLACH AND GERLACH: *Clinical and Pathological Applications of Spectrum Analysis*. Adam Hilger, Ltd., London (1934).
- (6) LOHSE: *Can. J. Research* **12**, 519 (1935).
- (7) LUNDGÅRDH: *Die quantitative Spektralanalyse der Elemente*. Jena (1929).
- (8) TWYMAN AND HITCHEN: *Proc. Roy. Soc. London* **133A**, 72 (1931).
- (9) WAIBEL: *Z. tech. Physik* **11**, 454 (1934).
- (10) WEISER: *J. Phys. Chem.* **35**, 1 (1931).
- (11) WEISER AND MIDDLETON: *J. Phys. Chem.* **24**, 30, 630 (1920).
- (12) WEISER AND SHERRICK: *J. Phys. Chem.* **23**, 205 (1919).

¹ *Note added in proof:* It is apparent that the spectra reproduced will not show plainly lines which are clearly visible on the original plates; the statements made in paragraphs I, II, III, and IV will have to be considered as true for the original plates.

VAPOR PRESSURE-WATER CONTENT RELATIONS FOR CERTAIN TYPICAL SOIL COLLOIDS¹

LYLE T. ALEXANDER

Bureau of Chemistry and Soils, U. S. Department of Agriculture, Washington, D. C.

AND

M. M. HARING

Department of Chemistry, University of Maryland, College Park, Maryland

Received June 20, 1935

Several attempts have been made to utilize the information obtained by allowing air-dry soil to absorb moisture at various relative humidities. The water absorbed by soil colloids when allowed to come to equilibrium over a sulfuric acid-water mixture containing 3.3 per cent sulfuric acid by weight has been made the basis for a method of estimating the quantity of colloid present in a soil (6). The water held under this condition (99 per cent relative humidity) falls below the hygroscopic coefficient. The British soil workers (8) have also used a determination of the moisture held at 50 per cent relative humidity as a criterion of soil properties. More recently, workers in the Bureau of Chemistry and Soils of the United States Department of Agriculture (5) have made determinations of the amounts of water held over sulfuric acid-water mixtures of various concentrations by different soil colloids. An attempt was made to correlate the ratios between some of the values so obtained with the chemical composition of the soil.

The vapor pressure-water content curves of a number of soils have been studied by Thomas (13, 14) and by Puri, Crowther, and Keen (11). They covered the entire range from oven-dry at 105°C. to saturation. It was found in both investigations that an inflection point in the curves occurred near 50 per cent of the vapor pressure of pure water. No breaks were found; this indicated no sudden change in the nature of the forces holding the water. Puri, Crowther, and Keen reached the conclusion that the curves were all of the same type, but that the general slopes of the curves were decreased with increases of clay and organic matter content. Thomas

¹ Abstracted from a thesis submitted by Lyle T. Alexander to the Graduate School of the University of Maryland in partial fulfillment of the requirements for the degree of Doctor of Philosophy, May, 1935.

Presented at the Twelfth Colloid Symposium, held at Ithaca, New York, June 20-22, 1935.

also reached the conclusion that the slope of the curve is influenced by the quantity of fine material present, but concluded that the organic matter played a minor rôle in water vapor absorption. Brown and Byers (5) and also Anderson and Mattson (3) have called attention to the correlation between the avidity of a soil colloid for water and its chemical constitution. Since it has been shown that the coarser fractions of a soil only serve as a framework or as diluting material for the colloid, it seemed advisable to study the colloid extracted from the soil rather than the soil itself. This would eliminate the variable factor mentioned by Puri, Keen, and Crowther concerning the change in slope of the vapor pressure curve with clay content.

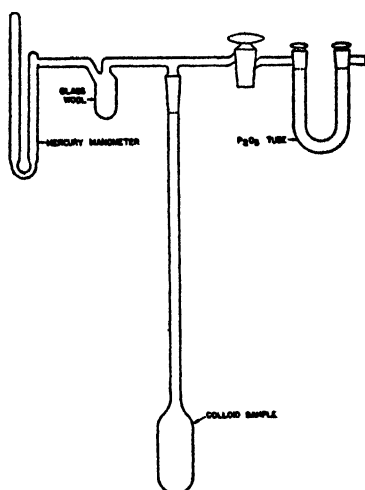


FIG. 1. Vapor pressure apparatus

EXPERIMENTAL

The soils selected for this study represent a wide range of progressive weathering. The Barnes soil is a black dry land grass soil from North Dakota. It has been formed from calcareous glacial till. It has not been subjected to severe hydrolysis because of the low rainfall.

The Carrington soil is a fertile prairie soil of Iowa. Like the Barnes soil, it has been developed from calcareous glacial till, but under conditions of more rainfall, and therefore its degree of hydrolysis is greater.

The Miami, a gray-brown podsollic soil from Indiana, has been developed under somewhat higher rainfall than the Carrington. This is a timber soil and not a grassland one.

The fourth soil selected is the Cecil, a red soil from North Carolina, that has been developed from decomposed granites and gneisses under condi-

TABLE 1

Relation between the vapor pressure and water content of the Barnes colloid at 25°C.
 Sample No. 10307. Dry weight of sample = 9.101 g.

VAPOR PRESSURE	WEIGHT OF WATER LOST BY SAMPLE	PER CENT OF WATER IN SAMPLE	VAPOR PRESSURE	WEIGHT OF WATER LOST BY SAMPLE	PER CENT OF WATER IN SAMPLE
<i>mm. Hg</i>	<i>grams</i>	<i>per cent</i>	<i>mm. Hg</i>	<i>grams</i>	<i>per cent</i>
23.1	0.031	33.4	12.8	1.641	15.7
22.6	0.156	32.0	11.8	1.702	15.0
22.6	0.259	30.9	10.9	1.760	14.4
22.1	0.352	29.8	9.9	1.825	13.6
21.8	0.498	28.2	9.3	1.869	13.2
21.2	0.623	26.9	8.7	1.902	12.8
21.0	0.647	26.6	8.0	1.961	12.1
20.6	0.722	25.8	7.0	2.027	11.4
19.9	0.856	24.3	5.9	2.112	10.5
19.5	0.934	23.4	5.3	2.143	10.1
19.0	1.020	22.5	4.0	2.283	8.6
18.5	1.072	21.9	2.8	2.363	7.7
18.1	1.134	21.2	1.8	2.478	6.5
17.3	1.200	20.5	1.0	2.583	5.3
16.6	1.280	19.6	0.0	3.069	0.0
15.7	1.368	18.7	Additional point by desiccator method		
15.4	1.459	17.7			
14.1	1.560	16.6	23.2		35.4
13.2	1.619	15.9			

TABLE 2

Relation between the vapor pressure and water content of the Carrington colloid at 25°C.
 Sample No. 10084. Dry weight of sample = 8.977 g.

VAPOR PRESSURE	WEIGHT OF WATER LOST BY SAMPLE	PER CENT OF WATER IN SAMPLE	VAPOR PRESSURE	WEIGHT OF WATER LOST BY SAMPLE	PER CENT OF WATER IN SAMPLE
<i>mm. Hg</i>	<i>grams</i>	<i>per cent</i>	<i>mm. Hg</i>	<i>grams</i>	<i>per cent</i>
25.7	0.019	26.9	10.1	1.621	9.0
23.1	0.137	25.6	6.5	1.819	6.8
22.4	0.293	23.8	5.3	1.898	6.0
22.1	0.499	21.6	1.4	2.130	3.4
20.7	0.731	19.0	1.2	2.158	3.1
19.0	0.974	16.6	0.0	2.432	0.0
16.4	1.233	13.4	Additional point by desiccator method		
15.8	1.343	12.2			
12.2	1.492	10.5	23.3		26.2

tions of high rainfall and temperature, where the hydrolysis has been severe.

The colloid was so extracted that the upper limit of particle size was

TABLE 3

Relation between the vapor pressure and water content of the Miami colloid at 25°C.
 Sample No. 10342. Dry weight of sample = 9.437 g.

VAPOR PRESSURE	WEIGHT OF WATER LOST BY SAMPLE	PER CENT OF WATER IN SAMPLE	VAPOR PRESSURE	WEIGHT OF WATER LOST BY SAMPLE	PER CENT OF WATER IN SAMPLE
mm. Hg	grams	per cent	mm. Hg	grams	per cent
24.9	0.134	19.9	11.4	1.443	6.0
22.7	0.212	19.1	10.4	1.456	5.8
22.7	0.296	18.2	9.6	1.515	5.2
21.8	0.346	17.6	7.8	1.561	4.8
21.7	0.403	17.0	6.3	1.597	4.4
21.9	0.523	15.8	4.7	1.659	3.7
21.5	0.606	14.9	4.4	1.672	3.6
20.9	0.692	14.0	3.6	1.703	3.3
20.3	0.820	12.6	3.0	1.737	2.9
20.3	0.895	11.8	2.5	1.744	2.8
19.6	0.956	11.2	1.9	1.781	2.4
18.8	1.062	10.0	1.1	1.845	1.8
18.0	1.125	9.4	0.0	2.013	0.0
16.9	1.181	8.8	Additional point by desiccator method		
15.7	1.257	8.0			
15.2	1.309	7.4	23.3		25.0
13.7	1.376	6.7			

TABLE 4

Relation between the vapor pressure and water content of the Cecil colloid at 25°C.
 Sample No. 9415. Dry weight of sample = 9.910 g.

VAPOR PRESSURE	WEIGHT OF WATER LOST BY SAMPLE	PER CENT OF WATER IN SAMPLE	VAPOR PRESSURE	WEIGHT OF WATER LOST BY SAMPLE	PER CENT OF WATER IN SAMPLE
mm. Hg	grams	per cent	mm. Hg	grams	per cent
24.3	0.096	22.3	10.2	2.014	3.0
22.7	0.274	20.5	8.3	2.055	2.5
22.7	0.394	19.3	7.0	2.085	2.3
22.4	0.529	17.9	5.9	2.106	2.0
22.1	0.669	16.5	5.0	2.130	1.8
22.1	0.794	15.3	3.7	2.162	1.5
22.1	0.947	13.7	2.9	2.182	1.3
21.7	1.071	12.5	2.3	2.187	1.2
21.2	1.223	11.0	1.4	2.214	1.0
20.4	1.360	9.6	1.1	2.229	0.8
20.0	1.469	8.5	0.9	2.246	0.6
19.8	1.587	7.2	0.9	2.262	0.4
18.2	1.708	6.0	0.0	2.309	0.0
17.1	1.803	5.1	Additional point by desiccator method		
14.3	1.909	4.0			
12.3	1.966	3.4	23.3		27.9

about 0.3 micron in diameter (5). The colloid was air-dried at room temperature to avoid any irreversible dehydration at the elevated temperature.

The apparatus used for determining the detailed vapor pressure–water composition curves is essentially that used by Wales and Nelson (15). A diagrammatic representation of it is shown in figure 1.

After a 10-g. sample of air-dry colloid ground to pass a 100-mesh sieve had been placed in an evacuated desiccator over 3.3 per cent sulfuric acid for a period of five days, the sample was weighed and transferred to the bulb of the apparatus shown in figure 1. The apparatus was then evacuated through the phosphorus pentoxide tube until about 0.1 g. of water was collected. The stopcocks were closed and the whole apparatus allowed to

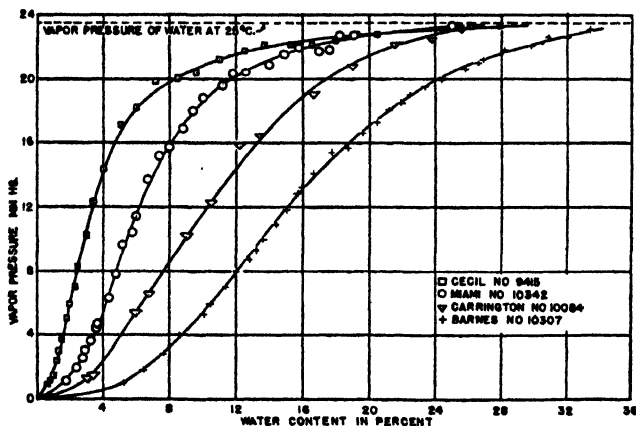


FIG. 2. Water content relation for soil colloids at 25°C.

stand until equilibrium was reached. The phosphorus pentoxide tube was then weighed, and the difference in level of the two legs of the manometer read by means of a cathetometer. The apparatus was again evacuated and the process repeated. The experimental data obtained by this method are given in tables 1 to 4. Also given in these tables is the value for water held, at 25°C., by the colloid in an evacuated desiccator containing aqueous sulfuric acid, with a water vapor pressure of 23.3 mm. Hg. Most of the values were taken after allowing twenty-four hours for equilibrium to be reached. Although this may not be a real equilibrium point, no further change in pressure could be noted by allowing three or four days time.

The curves for the four soil colloids are shown in figure 2. These are all of the same general form. They are similar to the curves for gelatin given by Katz (7) and to those for wood found by Stamm and Loughborough (12). They are also similar to that for aqueous sulfuric acid. Data are available in the International Critical Tables for the sulfuric acid. The first few values on each curve are undoubtedly too high because of

removal of adsorbed air. The very low ones are a bit uncertain because the mercury manometer was not sensitive to small changes in pressure in the very low range.

MATHEMATICAL EXPRESSIONS FOR THE CURVES

Katz (7) expressed the vapor pressure-water content relation for an elastic gel by the equation

$$-\frac{RT}{V_0} \ln h = \frac{\alpha\beta}{(\beta - \alpha)^2}$$

where α and β are empirical constants, h is the ratio of the vapor pressure of the gel to that of pure water at the same temperature, α is the water content in grams, per gram of dry colloid, V_0 is the specific volume of water, and R and T have their usual significance.

This equation was tested to see if it would fit the curves for the soil colloids studied. The results were not satisfactory. However, a satisfactory equation for two of the colloids may be obtained as follows. Consider the reaction



where x is always less than y . The decrease in free energy for this reaction may be obtained from

$$\Delta F = \frac{RT}{M} \ln \frac{P}{P_0} \quad (1)$$

where M is the molecular weight of water, P is the equilibrium pressure of the system, P_0 is the vapor pressure of water at the same temperature, and ΔF is the free energy decrease at this temperature when 1 g. of water is added to an infinite amount of soil colloid ($x\text{H}_2\text{O}$).

These values have been calculated for vapor pressures taken from the curves of figure 2, and are presented graphically in figure 3.

As a rule such curves (figure 3) will be found to fit an equation of the type

$$y = ae^{-bx} \quad (2)$$

where a and b are constants and y and x represent the ordinates and abscissae, respectively, and $e = 2.7183$. Letting $x = \text{percentage of water in sample}$ and $y = \Delta F$, we have

$$\Delta F = ae^{-bx} \quad (3)$$

Equating equation 1 and equation 3

$$\frac{RT}{M} \ln \frac{P}{P_0} = ae^{-bx} \quad (4)$$

Since R , T , M , and a are constants, we may combine them with the conversion factor to Briggsian logarithms and obtain

$$\log \frac{P}{P_0} = a'e^{-bx} \quad (5)$$

a' and b may be evaluated by throwing the equation into the logarithmic form

$$\log \log \frac{P}{P_0} = \log a' - bx \log e \quad (6)$$

$$\log \log \frac{P}{P_0} = \log a' - 0.4343 bx \quad (7)$$

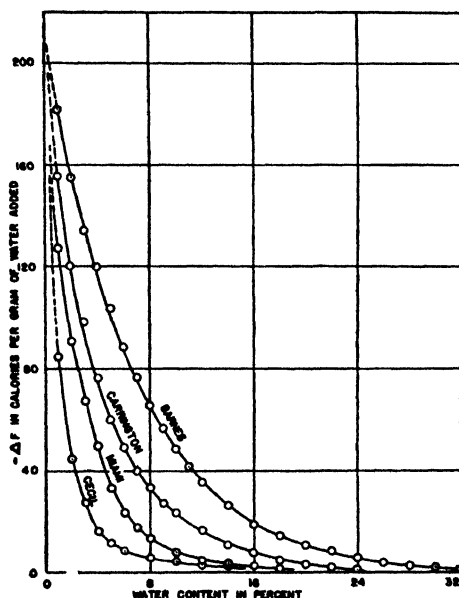


FIG. 3. Change in free energy of soil colloids as a function of water content at 25°C.

a' of course = $\frac{Ma}{2.303RT}$; a' (and therefore a) and b may then be evaluated by plotting $\log \log \frac{P}{P_0}$ against x or by plotting $\log \frac{P}{P_0}$ on semi-log paper against x . $\log a'$ will be the intercept on the y axis and $-0.4343b$ the slope. Curves for the four soil colloids studied, plotted by the first method, are given in figure 4. Straight portions are found for all the types, especially at lower water percentages. Equations for the straight portions of

each are given below. They are valid, naturally, only for colloids of water content lying on the straight portion.

$$\log \frac{P}{P_0} = 2.82e^{-0.148x} \quad (\text{Barnes})$$

$$\log \frac{P}{P_0} = 2.32e^{-0.205x} \quad (\text{Carrington})$$

$$\log \frac{P}{P_0} = 2.21e^{-0.311x} \quad (\text{Miami})$$

$$\log \frac{P}{P_0} = 1.15e^{-0.491x} \quad (\text{Cecil})$$

Possible explanations for the failure to obtain straight lines at higher water contents will be offered later.

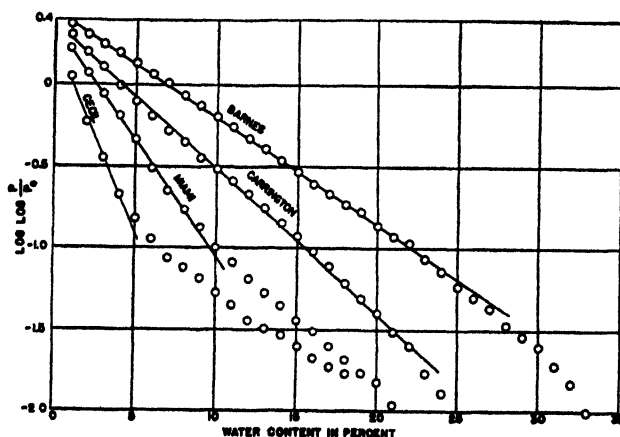


FIG. 4. Log log of vapor pressure ratio as a function of water content at 25°C.

We may obtain the total free energy change for an addition of an amount of water corresponding to 99 per cent of saturation. These values are obtained by determining the area under the curves shown in figure 3. The values obtained are given below.

	ΔF IN CALORIES PER GRAM OF COLLOID	ΔH IN CALORIES PER GRAM OF COLLOID
Barnes.....	14	22
Carrington.....	9	17
Miami.....	6	14
Cecil.....	3	6

The values for ΔH were obtained by measuring the heat of wetting of the soil colloids according to the method of Anderson (1), except that the samples were dried over concentrated sulfuric acid at 25°C. instead of in the oven at 105°C.

RELATION TO COLLOID COMPOSITION

In recent years chemists have discovered an important relation between the chemical composition of the colloid of a soil and its field characteristics. This relation is sometimes obscured by the presence of unweathered minerals in the extracted colloid. Such minerals are abundant in most soils (9).

Since unweathered ground minerals such as orthoclase do not hold water appreciably in the hygroscopic range, they should, if present as an impurity, serve merely as a diluent, and hence affect the vapor pressure curves only slightly. An examination of the curves in figure 2 shows that the Miami falls nicely into its proper relation between the Carrington and Cecil and not between the Barnes and Carrington as its silica sesquioxide and silica alumina ratios would predict.

The differentiation shown by this family of curves between the four groups of soils covered in this investigation is sharp and of even distribution. It appears that the hygroscopic moisture of the colloid is a characteristic function of the factors which determine the field characteristics of the soil. Further investigation may reveal some curves out of place, just as some of the ratios are out of place, but this will not invalidate the use of these curves as criteria of soil properties.

THE NATURE OF THE HYGROSCOPIC WATER

The data shown in this paper indicate that the hygroscopic water of the soil colloids is held in a similar manner to water of swelling in gelatin and in wood.

Probably the most illuminating treatment of hygroscopic water in elastic gels is that of Peirce (10). He proposes a "two-phase" theory of absorption of water by cotton cellulose, which has water content-vapor pressure isothermals very similar to those of soil colloids.

According to the Peirce theory the hygroscopic water can be considered as occurring in two different phases, or states, on the cellulose. The first of these is the *a* phase which is held to be chemically bound by the hydroxyl groups of the hexose units of the cellulose. The second or *b* phase is made up of the water molecules attracted by the water molecules of the *a* phase and by the colloid surface which is not reactive toward water. From theoretical considerations he arrives at the following formula for the vapor pressure-water content isotherms for cotton and starch

$$1 - \frac{P}{P_0} = (1 - kC_a)e^{-bC_b}$$

where P is the water vapor pressure of the cellulose (xH_2O), P_0 is the vapor pressure of water at the same temperature, k is a constant characteristic for each sample, C_a is the concentration of moisture in the a phase, B is another constant characteristic of each sample, and C_b is the concentration of water in the b phase.

This equation is similar in many respects to the equation arrived at on page 201 for the soil colloids. Peirce pointed out that the equation would be applicable only to pure substances. It is probable that the failure of the vapor pressure–water content curves to rectify, as shown in figure 4, is due to some contaminating colloid which does not exert a noticeable lowering of the vapor pressure in the lower moisture content ranges, but which does make itself noticeable in the higher moisture content ranges. Iron oxide is a contaminant to which we might attribute this behavior.

If then we apply the two-phase theory of Peirce to soil colloids, we may picture the a phase water as being combined with the alumino silicic acid complex, with the tendency toward further hydration as the attracting force. The b phase water is held on the surface of the colloid not occupied by a phase water and as outer layers on the a phase water.

Concerning the a phase water, one must conclude that in the little hydrolyzed soils of the chernozem group the tendency to hydrate is very great, and that in the lateritic Cecil series the tendency is very small. The b phase water does not appear to be so much a function of the chemical composition of the colloid as of the surface. Further investigation is necessary to determine the quantitative relations between these two kinds of hygroscopic water.

This idea of the two kinds of hygroscopic water is easily harmonized with the work of Anderson (2) and of Bayer and Horner (4) on the effect of exchangeable ions on the hygroscopicity of colloids. It is interesting to note that the colloids having high base exchange capacities are the ones having much attraction for the a phase water. It is possible that the base exchange phenomena and absorption of a phase water are due to the same chemical affinity, that is, secondary valence, or it may be that the base exchange bases are held by primary valence bonds. Further investigations along this line would be necessary to decide which of these is responsible for the phenomena.

SUMMARY

1. A study has been made of the vapor pressure–water content curves of four typical soil colloids. The curves are shown to be characteristically different for the different soil groups.

2. The change of free energy as a function of water content has been calculated, and the total free energy change on wetting has been determined approximately.

3. An attempt has been made to correlate vapor pressure curves with soil classification.

4. Peirce's two-phase theory of water absorption by cellulose is used to picture the nature of the hygroscopic water of soil colloids.

REFERENCES

- (1) ANDERSON, M. S.: J. Agr. Research **28**, 927-35 (1924).
- (2) ANDERSON, M. S.: J. Agr. Research **38**, 565-84 (1929).
- (3) ANDERSON, M. S., AND MATTSO, S. A.: U. S. Dept. Agr. Bull. 1452 (1926).
- (4) BAYER, L. D., AND HORNER, GLEN M.: Soil Sci. **36**, 329-53 (1933).
- (5) BROWN, I. C., AND BYERS, H. G.: U. S. Dept. Agr. Tech. Bull. 319 (1932).
- (6) GILE, P. L., MIDDLETON, H. E., ROBINSON, W. O., FRY, W. H., AND ANDERSON, M. S.: U. S. Dept. Agr. Bull. 1193 (1924).
- (7) KATZ, J. R.: Die Gesetze der Quellung. Eine biochemische und kolloidchemische Studie. 1 Teil: Die Quellung in Wasser ohne Komplikation. Kolloidchem. Beihefte **9**, 1-182 (1917).
- (8) KEEN, BERNARD A.: The Physical Properties of the Soil. Longmans, Green and Co., New York (1931).
- (9) McCAUGHEY, W. J., AND FRY, W. H.: Bureau of Soils Bull. 91 (1913).
- (10) PEIRCE, F. T.: J. Textile Inst. **20**, T133-T150 (1929).
- (11) PURI, A. N., CROWTHER, E. M., AND KEEN, B. A.: J. Agr. Sci. **15**, 68-88 (1925).
- (12) STAMM, ALFRED J., AND LOUGHBOROUGH, W. KARL: J. Phys. Chem. **39**, 121-32 (1935).
- (13) THOMAS, MOYER D.: Soil Sci. **9**, 409-34 (1921).
- (14) THOMAS, MOYER D.: Soil Sci. **17**, 1-18 (1924).
- (15) WALES, H., AND NELSON, O. A.: J. Am. Chem. Soc. **45**, 1657-66 (1923).

STREAM POTENTIALS AND D. C. SURFACE CONDUCTIVITIES IN SMALL CAPILLARIES^{1,2}

H. L. WHITE, BETTY MONAGHAN, AND FRANK URBAN

*Department of Physiology and Department of Biological Chemistry, Washington
University School of Medicine, St. Louis, Missouri*

Received June 20, 1935

A few years ago (8) we reported that the stream potentials of glass capillaries decrease with capillary diameter, being for 5-micra capillaries from 0 to 25 per cent of the normal with 2.5 and 5×10^{-4} *M* potassium chloride, the normal being defined as that found with large capillaries. These findings are believed to be more nearly correct than the earlier report (6) that the stream potential of 5-micra capillaries was, with 5×10^{-4} *M* potassium chloride, about 75 per cent of normal; the earlier findings were presumably due to technical imperfections. We are now reporting on a larger series of measurements on capillaries from 333- to 4.1-micra diameter, with solutions ranging from water to 10^{-2} *M* potassium chloride. The present findings confirm, with some qualifications, and extend those of White, Urban, and Van Atta.

METHODS

The condenser arrangement used in the earlier work was replaced by a vacuum tube amplifier (FP54) for measuring both stream potentials and capillary resistances. The apparatus is shown in figure 1. The amplifier is shielded by its metal box, the remainder of the apparatus by a large copper screen cage. Due precautions as to insulation were observed. With the top of switch A to the left, grid grounded, the plate current is balanced to zero by adjustment of R_2 and R_4 . With the switch in the middle position the plate current is again brought to zero by the potentiometer, whose reading gives the potential to be measured, in this case the stream potential. With the top of switch A to the right the voltage drop across R_s is measured, and from this is calculated the resistance of the capillary. One or more dry cells of known voltage may be put in series with R_s and the capillary to measure capillary resistance, or the stream potential alone may be used; the same result is obtained with both methods. If a dry

¹ Presented before the Twelfth Colloid Symposium, held at Ithaca, New York, June 20-22, 1935.

² Aided by a grant made by the Rockefeller Foundation to Washington University for research in science.

cell of known voltage is put into the electrode circuit with switch A in the middle position, the measured voltage is the sum of stream potential and added voltage; this procedure was frequently used as a check. The galvanometer G has a current sensitivity of 1.85×10^{-8} amperes per millimeter; the voltage sensitivity of the amplifier is about 0.002 volt per millimeter with the lower resistances, and about 0.006 volt per millimeter with the highest (above 10^{11} ohms).

The standard high resistances, R_s , are of two types,—gold or platinum films sputtered on glass rods (5) and carbon impregnations; a series ranging

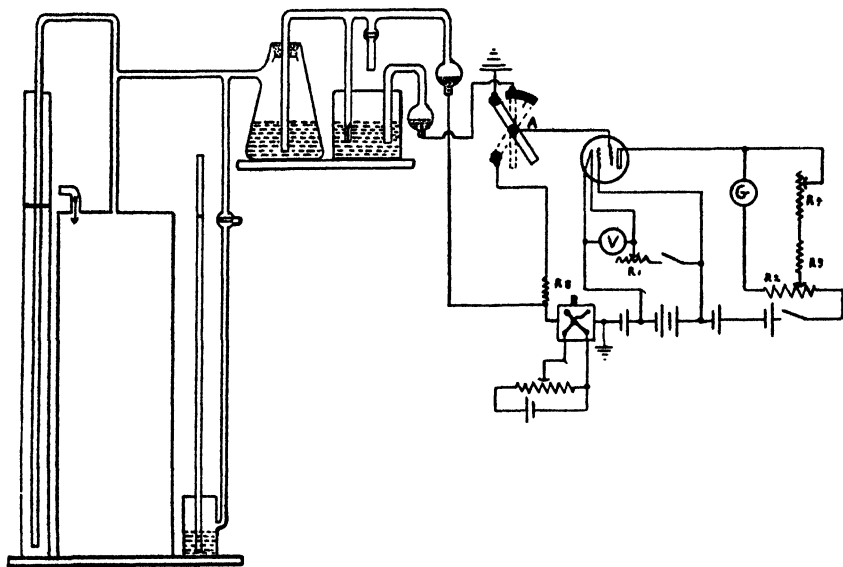


FIG. 1. Apparatus for measuring stream potentials and conductivity. A, high resistance switch; B, reversing switch; V, voltmeter; G, galvanometer; R_1 , 20 ohms; R_2 , 400 ohms; R_3 , 20,000 ohms; R_4 , 11,000 ohms; R_s , standard high resistance.

from 2.18×10^8 to 1.03×10^{11} ohms was employed. They were supplied by the Department of Physics, and we are indebted to Dr. G. M. Webb of that department for their initial measurements. The carbon type usually show some change in resistance with change in applied voltage; we have therefore calibrated them for the range of voltages employed. For each determination a standard was chosen as near the value of the unknown as possible; the ratio was usually less than 2 and never more than 3. Our stream potential measurements are in error by not more than 0.002 volt, and the capillary resistances by not more than 1 per cent with resistances less than 10^{10} ohms and not more than 2 per cent with resistances above 10^{10} ohms.

Capillary lengths were measured with micrometer calipers; their cross-sectional area was calculated from the observed resistance when filled with $M/10$ potassium chloride. In some cases diameters were checked by microscopic measurement; agreement with the other method was usually within 1 or 2 per cent, but in all cases the results of the first method were taken. Using the data of capillary dimensions and of observed capillary resistance with dilute solutions the net specific conductivity of the latter in the capillaries was calculated, designated κ_{cap} in the tables.

Two methods of treatment were used with the capillaries. With the first, treatment a, the capillaries were left in chromic acid overnight and then subjected to prolonged rinsing with distilled water. With the second, treatment b, the capillaries were immersed in boiling distilled water for one hour and then washed in distilled water. No consistent differences in the results of these two treatments were observed. The water used in treating the capillaries and in making up the potassium chloride solutions was double distilled, first from an electrical laboratory still and then from an all-Pyrex still to which was added a little Nessler's solution. The specific conductivity of this water ranged from 0.9 to 2.0×10^{-6} mhos.

RESULTS

Stream potentials

In the first series capillary resistances were not measured, and therefore specific conductivities in the capillaries not determined. These will not differ significantly from specific bulk conductivities, κ_{sol} , with the larger capillaries and higher concentrations of table 1, since here surface conductivity is negligible. With the lower concentrations, however, there will be an appreciable surface conductivity except with the largest (333 micra) capillary, the ratio of surface to bulk conductivity of course increasing as capillary diameter decreases. Therefore zeta is shown in table 1 with concentrations of $1 \times 10^{-4} M$ and less only for the largest capillary; with the other capillaries at these low concentrations, specific conductivity in the capillary, κ_{cap} , is to an increasing degree greater than κ_{sol} as capillary diameter decreases. Table 1 shows that the stream potential, E/P , falls with decreasing capillary diameter and that the effect of diameter is greater the more dilute the solution. With concentrations of $5 \times 10^{-4} M$ and greater the size effect is no longer appreciable above diameters of 18 micra. While we cannot make a positive statement as regards these particular experiments, since we do not have resistance measurements here, it seems probable, on the basis of many other measurements of surface conductivity, that the size effect on E/P here is due largely to the effect of increased conductivity in the smaller capillaries.

The reproducibility of results with the smallest capillaries is not suffi-

ciently close to permit an evaluation of the effect of electrosmotic retardation of velocity in the double layer, as discussed by Reichardt (4), which would be a further contributing factor in the lowering of E/P .

The κR effect, discussed by Müller and Abramson (1) in connection with electrophoresis and later applied by Komagata (2) to the stream potential

TABLE 1
Stream potentials without resistance measurements

DATE	SOLUTION	κ_{sol}	CAPILLARY DIAMETER	E/P	PER CENT OF NORMAL	ZETA
		$\text{mhos} \times 10^{-4}$	<i>micra</i>	<i>mv./cm. Hg</i>		<i>mv.</i>
Nov. 6	Water	1.87	333	734	100	132
			85.4	555	76	
			39.0	258	35	
			12.0	157	21	
			5.78	25	3	
Nov. 7	$10^{-3} M \text{ KCl}$	3.71	333	201	100	107
			85.4	268	89	
			39.0	132	44	
			12.0	96	32	
			5.78	6	2	
Nov. 8	$10^{-4} M \text{ KCl}$	16.6	333	71.2	100	114
			85.4	71.4	100	
			39.4	68.1	95	
			12.0	48.3	68	
July 18	$5 \times 10^{-4} M \text{ KCl}$	76.7	333	14.0		103 (average)
			97.6	15.2		
			58.0	14.5		
			40.5	13.3		
			18.6	14.0		
July 14	$10^{-3} M \text{ KCl}$	149	97.6	6.8		99 (average)
			58.0	7.2		
			40.5	7.2		
			18.6	6.7		
July 20	$10^{-3} M \text{ KCl}$	1413	58.0	0.28		36 (average)
			40.5	0.26		

problem, is so small as not to be measurable. Komagata's statement (ref. 2, p. 37) that this effect could explain the observed drop in stream potential with diminishing capillary size is invalid for three reasons. First, his table of limiting values of radius, i.e., radius of capillary below which the effect becomes significant, shows all the figures with ten times the cor-

rect value, as can readily be seen by substituting values for κ . Thus, where he says a capillary of 24.6-micra radius would show a fall of 1.5 per cent in stream potential with 10^{-4} M potassium chloride, this is really true

TABLE 2
Results with 1×10^{-4} M potassium chloride

CAPILLARY DIAMETER	DATE	TREATMENT	κ_{sol}	E/P	κ_{cap}	ZETA	Λ_0
micra			$\text{mhos} \times 10^{-3}$	mv./cm. Hg	$\text{mhos} \times 10^{-3}$	mv.	$\text{mhos} \times 10^{-3}$
38.6	May 9	a	1.65	68.7	1.80	117	1.50
	May 10	a	1.67	73.0	1.81	125	1.39
	May 13	a	1.67	64.8	1.83	112	1.58
	May 15	a	1.71	70.2	1.84	122	1.34
	May 16	a	1.71	68.1	1.81	117	1.01
	May 22	b	1.66	60.0	1.76	100	1.10
	May 23	b	1.66	65.4	1.76	109	1.10
12.0	May 9	a	1.65	56.2	2.00	106	1.03
	May 13	a	1.67	14.4	1.97	31	0.89
	May 16	a	1.71	17.0	2.04	33	0.98
				15.9	2.03	31	0.95
	May 22	b	1.66	13.1	1.92	23	0.77
5.4	May 31	a	1.77	2.2	3.26	7	1.85
	June 1	b	1.77	>1	2.90	>1	1.44
4.1	May 9	a	1.65	42.2	3.23	129	1.65
	May 10	a	1.67	38.4	3.23	117	1.63
	May 11	a	1.67	35.0	3.11	103	1.50
	May 17	a	1.71	24.2	2.85	65	1.19
	May 18	a	1.69	20.6	2.50	49	0.85
				18.4 eq	2.40	42	0.74
	May 21	a	1.67	34.1	2.92	94	1.30
				32.8	2.87	89	1.25
				32.2	2.82	86	1.20
				31.1	2.73	80	1.10
				29.9	2.71	77	1.07
				29.5	2.71	76	1.07
				28.3	2.60	70	0.97
	May 22	b	1.66	26.8 eq	2.66	68	1.04
	June 1	b	1.77	31.0	2.34	39	0.60
				17.7 eq			

for a 2.46-micra radius. Since no one ever has been able to measure stream potentials on capillaries of 5-micra diameter with a reproducibility within 1.5 per cent, the matter is not at present susceptible

to experimental investigation. Second, he quotes White, Urban, and Krick as having used $5 \times 10^{-5} M$ potassium chloride, where the effect would be somewhat greater, whereas we used $5 \times 10^{-4} M$ potassium chloride. Third, we now know that the stream potential in 5-micra capillaries is usually reduced to an even greater extent than reported by White, Urban, and Krick. The matter may be summed up by the statement that the Komagata effect is entirely negligible and in no way able to account for the observed diminution in stream potential with decreasing capillary size. Of course, with pores of ultramicroscopic size, as in colloidion and cellophane membranes, the effect no doubt is important, particularly with dilute solutions.

In the experiments of tables 2 and 3 capillary resistances were measured, making possible calculation of κ_{cap} and of zeta. E/P of the smaller (4.1 and 12 micra) capillaries is originally reduced to about the extent that

TABLE 3
Results with $5 \times 10^{-4} M$ potassium chloride

CAPILLARY DIAMETER	DATE	TREATMENT	κ_{sol}	E/P	κ_{cap}	ZETA	κ_s
<i>micra</i>			<i>mhos $\times 10^{-5}$</i>	<i>mv./cm. Hg</i>	<i>mhos $\times 10^{-5}$</i>	<i>mv.</i>	<i>mhos $\times 10^{-5}$</i>
5.4	June 3	a	7.67	>1	8.80	>1	1.39
	June 6	b	7.67	>1	8.70	>1	1.28
4.1	May 2	a	7.66	12.6	9.45	109	1.87
	May 3	a	7.66	12.0	9.20	104	1.63
	May 8	a	7.66	11.5	9.13	99	1.55
	June 3	a	7.67	5.7	7.97	43	0.31
	June 6	b	7.67	4.5	7.89	37	0.23

κ_{cap} is increased over κ_{sol} , i.e., zeta is about normal. In general, however, E/P and zeta fall with time; this tendency appears to be greater the smaller the capillary, although the large ones also show some fall with time. The "eq" after some of the figures in table 2 designates that these were stable or equilibrium values for these dates, i.e., that no further fall occurred during several hours. Some exceptions may be found to almost any general statement about capillary behavior if one makes enough measurements. Some small capillaries, as the 5.4-micra capillary of tables 2 and 3, never show much stream potential, even when new. This may be because of a localized constriction which cannot be recognized by our methods of measurement. It thus appears that cylindrical small capillaries may early in usage show a normal zeta, which means for a 5-micra capillary with $1 \times 10^{-4} M$ potassium chloride an E/P of about 50 per cent the normal value, but that zeta usually falls with time so that E/P becomes from 5 to 30 per cent of normal. The operation of factors which might be expected

to lower zeta by not more than 10 or 15 per cent could hardly be recognized.

Surface conductivity

Data on specific surface conductivity are also given in tables 2 and 3. The calculated values of the capillary resistances with the dilute solutions are obtained from the capillary dimensions and the observed specific bulk conductivities of the dilute solutions, which of course include the conductivity of the water. From these data and from the observed capillary resistances with the dilute solutions the specific surface conductivities are calculated. The results are more reliable with 1×10^{-4} than with 5×10^{-4} *M* potassium chloride, since with the former surface conductivity is a considerably higher fraction of total conductivity. While the tables show that the normal specific surface conductivity with 1×10^{-4} *M* potassium chloride is only slightly less than with 5×10^{-4} *M*, we do not insist that this represents the real truth, because of the probable error in the latter measurements. We believe, however, that the findings permit the conclusion that within this range of concentrations changes in specific surface conductivity must be considerably less than changes in bulk conductivity. The magnitude of the present values for specific surface conductivity with 5×10^{-4} *M* potassium chloride agrees well with the value of 2.2×10^{-9} mhos per cm.² reported by White, Urban, and Van Atta (7).

Many measurements of surface conductivity have been made while the solution was being forced through the capillary under pressure up to 60 cm. of mercury, and many others with no applied pressure, the liquid in the flask and in the outer beaker in this case being carefully brought to the same level. We have never seen any evidence that the flow of liquid has any effect on surface conductivity. Surface conductivity remains the same, for at least an hour after pressure is released, as it was while the pressure was on.³ Whatever effect electrosmotic movement may have in disturbing the structure of the double layer, as postulated by McBain and Foster (3), would of course still be operative with the pressure released.

Correlation between surface conductivity and zeta

The findings on the smaller capillaries, other than the 5.4-micra capillary show a correlation between the magnitudes of zeta and of surface conductivity. No correlation exists with the 5.4-micra capillary because it was incapable at any time of showing anywhere near a normal stream potential, probably because of a localized constriction. It appears that

³ This, of course, does not answer McBain and Foster's (3) objection that under these conditions surface conductivity, although present, is masked by a corresponding depletion of bulk solution in the capillary. We feel that the question must remain open for the present.

variations in double layer charge density, due to spontaneous variations in the properties of the surface, are reflected both in stream potential and in surface conductivity. This correlation in a given capillary was not detected by White, Urban, and Van Atta (8), because determinations both of stream potential and of surface conductivity were not made on capillaries smaller than 18 micra, where no great accuracy in surface conductivity measurements can be attained with $5 \times 10^{-4} M$ potassium chloride.

SUMMARY

1. The stream potential, E/P , of glass capillaries falls off with decreasing capillary diameter. This effect is due largely to the increased specific conductivity in the smaller capillaries, due to surface conductivity. While a retarding effect due to electrosmosis is no doubt present, the data do not permit its evaluation.

2. The κR effect, as applied by Komagata to stream potentials, is negligible except with pores of ultramicroscopic size.

3. The value of E/P with most capillaries falls with time; this is not due to an increase in conductivity but presumably to a decrease in zeta.

4. The normal specific surface conductivity, measured with direct current, of $1 \times 10^{-4} M$ potassium chloride at a Pyrex surface is about 1.5×10^{-9} mhos per cm.² and of $5 \times 10^{-4} M$ potassium chloride about 1.7×10^{-9} mhos per cm.²

5. Variations in zeta in a given capillary, as shown by variations in E/P , are also reflected in variations in specific surface conductivity.

REFERENCES

- (1) ABRAMSON, H.: J. Phys. Chem. **35**, 289 (1931).
- (2) KOMAGATA, S.: Researches Electrotech. Lab., p. 362 (1934).
- (3) MCBAIN, J. W., AND FOSTER, J. F.: J. Phys. Chem. **39**, 331 (1935).
- (4) REICHARDT, H.: Z. physik. Chem. **166A**, 433 (1933).
- (5) VAN ATTA, L. C.: Rev. Sci. Instruments **1**, 687 (1930).
- (6) WHITE, H. L., URBAN, F., AND KRICK, E. T.: J. Phys. Chem. **36**, 120 (1932).
- (7) WHITE, H. L., URBAN, F., AND VAN ATTA, E. A.: J. Phys. Chem. **36**, 1371 (1932).
- (8) WHITE, H. L., URBAN, F., AND VAN ATTA, E. A.: J. Phys. Chem. **36**, 3152 (1932).

ADSORPTION BY DIATOMACEOUS FILTERS¹

EARL J. HOAGLAND AND JOHN E. RUTZLER, JR.

Department of Chemistry, Cornell University, Ithaca, New York

Received June 20, 1935

While attempting to use a Berkefeld filter candle to remove mother liquor from a crystalline solid, it was found extremely difficult to draw air through the candle by means of a vacuum pump after it was wetted by the aqueous mother liquor. Then it was observed that after washing the wetted filter with acetone it passed air readily; the acetone did not dissolve out a determinable amount of solid. It was thought that an investigation of this phenomenon might yield better insight into the behavior of these diatomaceous filters, and perhaps reveal why pore size determinations by the bubble method are erratic (1). Despite the extensive use of diatomaceous earth (3), few studies of its adsorptive power appear to have been made.

All of the experiments were carried out with Berkefeld "N" diatomaceous candles, which are supposedly of medium pore size. The apparatus chain consisted of a vacuum pump connected to a 4-liter round-bottom flask which was in turn connected, by means of a T-tube, to a manometer and a 1-liter suction flask; between pump and suction flask was a by-pass which allowed evacuation of the suction flask without disturbing the 4-liter flask. The candle and its glass reservoir were fitted into the top of the suction flask by means of a one-hole rubber stopper. In some experiments an air-tight connection was made between the open end of the candle reservoir and a Friederichs' gas-washing bottle to control partially the water vapor content of the air entering the diatomaceous candle. Each unit of the apparatus was separable from the rest by stopcocks.

The experiments were made by evacuating the system up to the Berkefeld candle, closing off the vacuum pump, opening the candle to the evacuated system, and reading the height of the mercury in the open arm of the manometer at regular intervals of time. From the height of the mercury in the open arm of the previously calibrated manometer and the atmospheric pressure, the pressure within the system was determined for each interval of time. The 4-liter flask was used in order to provide a reliable and duplicable pressure difference between the open side of the

¹ Presented at the Twelfth Colloid Symposium, held at Ithaca, New York, June 20-22, 1935.

candle and the evacuated side. In this manner runs were made using different candles and the same candle under different conditions.

The first run was made using a new candle which had not been in contact with water, in order to determine the rate of flow of air through dry diatomaceous earth for comparison later with the rate through moist earth. This is candle No. 1. The next four runs with candle No. 1 were made using water, absolute ethanol, absolute methanol, and carbon tetrachloride. The data are given in table 1. The candle was completely dried each time before tests were made; and it was soaked thoroughly with the liquid to be tested, in addition to running 100 cc. of the liquid through it in each case. The gas-washing bottle did not contain any liquid during the runs of table 1. In this and the other tables representative data only are presented. In each run from twenty-five to fifty observations were made; all of these

TABLE 1
Adsorption of liquids by candle No. 1

AIR		CARBON TETRACHLORIDE		ABSOLUTE ETHANOL		ABSOLUTE METHANOL		WATER	
Time	Pressure	Time	Pressure	Time	Pressure	Time	Pressure	Time	Pressure
<i>seconds</i>	<i>mm.</i>	<i>seconds</i>	<i>mm.</i>	<i>seconds</i>	<i>mm.</i>	<i>seconds</i>	<i>mm.</i>	<i>seconds</i>	<i>mm.</i>
15	184	10	54	10	46	10	73	30	94
30	241	20	88	20	90	20	128	210	38
45	464	30	118	30	129	30	168	510	57
60	545	40	148	40	161	40	202	810	84
75	607	50	181	50	190	50	235	1005	103
90	649	60	211	60	216	60	265	1200	124
105	680	70	245	70	241	70	291	1410	152
120	696	80	277	80	263	80	320	1605	169.5
135	709	90	312	90	292	90	348	1800	208
150	718	100	344	100	318	100	371	2010	240

points were used in plotting the curves of figures 1 and 2, and formed smooth curves.

Using candle No. 2, which was new at the start, a study was made of the differences in rate of air flow through candles wetted by aqueous solutions. The data are given in table 2. Distilled water was used in all cases. All solutions were 1.23 *M*, and in each case the gas-washing bottle was filled with the solution being tested and connected with the candle reservoir to guard against clogging the filter by deposition of solid salt in the pores. Just before each run the candle was kept in the boiling test liquid until no more air bubbles escaped from it, cooled to room temperature, and placed in the system. From the time of immersion in the boiling test liquid until the start of the run the candle was kept constantly in contact with the liquid, 50 cc. of the test liquid being run through the candle into the suc-

tion flask immediately prior to the start of the run. Using the by-pass around the 4-liter flask the suction flask was quickly evacuated again. The remaining liquid in the reservoir was then poured out and the run started. After each run hot distilled water was passed through the candle until the filtrate gave no test for the solute just used; then 1 liter more of hot distilled water was run through the candle, thus assuring the absence of the electrolyte.

The data from table 2 are plotted in figure 1, the pressures being the pressures within the system at the given times. The differences in the pressures for the various liquids at any given time are taken as measures

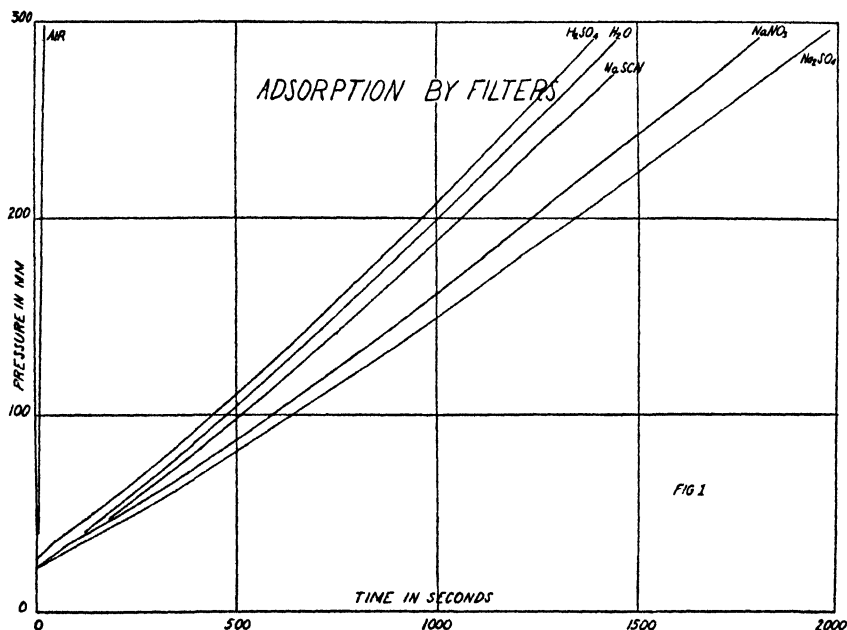


FIG. 1. Adsorption by filters

of the relative amounts of adsorption by the diatomaceous filters. The differences shown in figure 1 cannot be due to differences in vapor pressure, density, or viscosity, because they are not nearly in the correct order. The order of "clogging" of the candle was: sodium sulfate > sodium nitrate > sodium thiocyanate > water > sulfuric acid. If the effect were due entirely to changes in the water equilibrium, the order would either have to be the reverse of the above or the water curve would have to fall considerably further to the right. Experimental error is not a factor, because check runs made agreed to within 1.3 per cent.

Probably owing to the small amounts of electrolytes adsorbed by silica,

few data are found in the literature. Gore (6) determined the amounts of adsorption of a number of salts and acids at different concentrations by silica. Since diatomaceous earth is largely silica, it may be expected to behave roughly like silica. So far as one can determine from Gore's results, when recalculated for approximately molar solutions, the order of increasing adsorption for sodium salts is: sulfate < chloride < bromide < iodide. The molar sodium sulfate solution increased in concentration by 1.09 per cent. The other salts showed positive adsorption.

In so far as it is permissible to reason from silica to diatomaceous earth, the experiments of Gore provide what appears to be the soundest explanation of the present results. On this basis, sodium sulfate decreases the permeability of the candles to air mainly by an increase in the amount of water adsorbed by the diatomaceous earth. The effects produced by

TABLE 2
Adsorption of liquids by candle No. 2

WATER		SODIUM NITRATE		SODIUM THIOCYANATE		SODIUM SULFATE		SULFURIC ACID	
Time	Pressure	Time	Pressure	Time	Pressure	Time	Pressure	Time	Pressure
<i>seconds</i>	<i>mm.</i>	<i>seconds</i>	<i>mm.</i>	<i>seconds</i>	<i>mm.</i>	<i>seconds</i>	<i>mm.</i>	<i>seconds</i>	<i>mm.</i>
60	31.5	180	46.5	60	29.5	60	28.5	60	37.5
180	49.5	360	68.5	180	46.5	240	48.5	180	55.5
360	79.5	540	93.5	360	75.5	420	70.5	360	86.0
540	111.5	720	120.5	540	105.5	600	94.5	540	118.0
720	146.5	900	147.5	720	136.5	900	134.5	720	152.0
900	181.5	1080	175.5	900	170.5	1200	179.5	900	189.0
1080	217.5	1260	206.5	1080	207.5	1500	224.5	1080	227.0
1260	255.5	1440	234.5	1260	240.5	1800	268.5	1260	265.5
1440	291.5	1620	262.5	1380	262.5	1920	288.5	1380	291.5
1380	279.5	1800	292.5	1440	274.5	2040	306.5	1500	320.0

sodium nitrate and sodium thiocyanate appear to be due to adsorption of electrolyte superimposed on the adsorption of water; potassium nitrate was adsorbed considerably more (data not obtained for sodium nitrate) than the corresponding halogen salts in Gore's experiments. The position of the sulfuric acid curve in figure 1 is about what one would expect from the fact that Gore observed no effect with a molar solution of this acid; it falls closer to the water curve when a correction is introduced for a slight difference in temperature which existed. In all other cases the maximum difference in temperature was one degree from 27°C.

The data from table 1 are plotted in figure 2, curves 1, 2, and 3. Curve 1 was obtained by plotting the data for methanol, while curve 2 represents the data for ethanol and carbon tetrachloride, the two being so close together that they are represented by one curve. Curve 3 was obtained

by plotting the data for water in candle 1. Check runs agreed within 1 per cent. The main point of interest is the large difference between the curves for the organic liquids and that for water, the amounts of adsorption being of entirely different orders. Also there appears to be some specific adsorption as between the organic liquids, since vapor pressure differences do not entirely account for the results. In a differently arranged experiment, toluene and acetone behaved similarly to the above three organic liquids, did not differ much between themselves and, by comparison with water under those conditions, were only slightly adsorbed. Since the vapor pressure of toluene is about that of water, the differences between

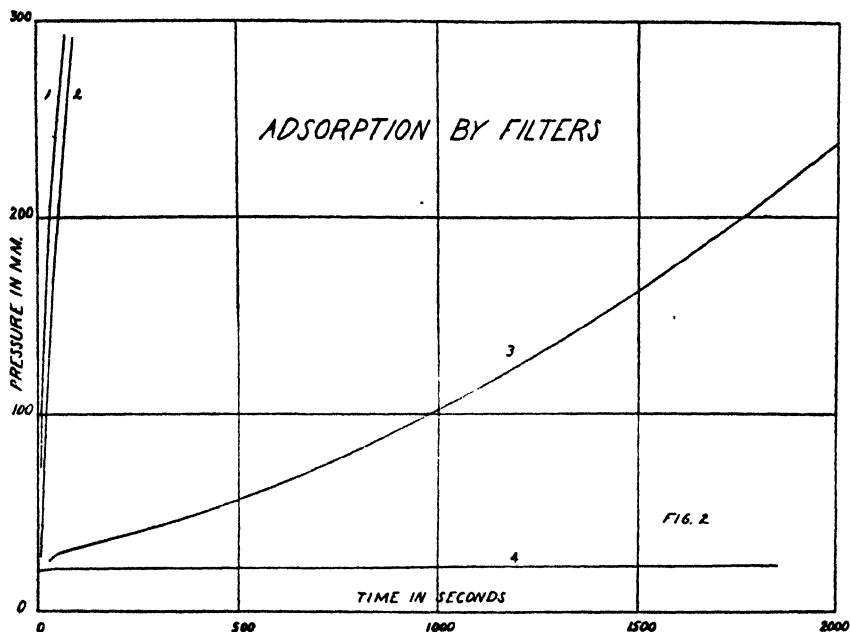


FIG. 2. Adsorption by filters

the behavior of the organic liquids and water cannot be accounted for on that basis. The air curve falls to the left of curve 1, of course.

Ewe (5) points out that filters for sera prepared from the same sample of kieselguhr treated in the same way show considerable variability in performance. This is probably due to differences in pore size and consequent differences in amounts of adsorption. Table 3 contains interesting data on the behavior of candle No. 3, also an "N" candle, toward water. The data are plotted in figure 2, curve 4. There is a tremendous difference in the adsorption of water by this candle and candle No. 2. With candle No. 3 the pressure in the system was below the vapor pressure of water at

that temperature for over thirty minutes. The candle was virtually plugged by adsorbed water. The water curve in figure 1 is different again, there being less adsorption than in either of the other two cases. These results were duplicated. From this it appears that identity of behavior is not to be expected as between any two given Berkefeld candles. It might be worthwhile for the bacteriologist to standardize his candles by the amount of water they will adsorb, using the above method.

Microscopic examination of candles No. 1, 2, and 3 revealed the reason for the differences in the amount of water adsorbed by them. It was found that with increasing adsorption of water there had been an increasing amount of destruction of the diatoms, probably during the process of manufacture. In other words, the fragments of the diatoms were smaller with increasing adsorption, which probably means smaller pore size and which certainly means an increased specific adsorbing surface.

TABLE 3
Adsorption of water by candle No. 3

TIME	PRESSURE	TIME	PRESSURE
<i>seconds</i>	<i>mm.</i>	<i>seconds</i>	<i>mm.</i>
15	20 5	1200	23 5
90	21 5	1800	23 5
240	21 5	3000	26 5
600	21 5	4500	28 0
900	22 5	7200	29 0

We can now see why pore size determinations in ultrafilters are erratic. Bechhold (2) gives two methods for the determination of pore sizes of ultrafilters, which he calls the air transpiration method and the rate of transfusion of water method, respectively. The air transpiration method falls down in such filters as the Berkefeld, where the water is strongly adsorbed; two different liquids would give two different values depending on their relative adsorptions, and two different filters would give different values which would express both a difference in pore size and a difference in adsorption. Measurements such as those of Einstein and Muhsam (4), in which ether was used instead of water, are probably free from this objection, because it is not to be expected that the ether is strongly adsorbed by the Berkefeld filter. In the rate of transfusion method no account is taken of the effect of adsorption. This method is defective to that extent. It seems clear that more concordant results on pore size should be obtained by the use of a non-adsorbed or slightly adsorbed liquid, and the pore size should be greater the less the adsorption.

The general results of this paper are as follows:

1. Diatomaceous earth adsorbs water strongly.

2. Berkefeld filters of the same rating show great variation in behavior when wetted by water, probably because the diatoms are crushed to different degrees.

3. Salts are adsorbed by diatomaceous earth, sodium thiocyanate being less strongly adsorbed than sodium nitrate.

4. There is quite strong negative adsorption of a sodium sulfate solution by the Berkefeld filter.

5. Organic liquids tested were adsorbed less than water.

6. A method is suggested for the evaluation of Berkefeld filters for bacteriological work.

7. Certain pore size determinations on ultrafilters are shown to be defective.

REFERENCES

- (1) BANCROFT: Applied Colloid Chemistry, p. 227. The McGraw-Hill Book Co., New York (1932).
- (2) BECHHOLD: Colloids in Biology and Medicine, p. 101 (1919).
- (3) CALVERT: Diatomaceous Earth (1930).
- (4) EINSTEIN AND MUSHAM: Deut. med. Wochschr. **49**, 1012 (1923).
- (5) EWE: J. Lab. Clin. Med. **5**, 538 (1920).
- (6) GORE: Chem. News **69**, 23 (1894).

ADSORPTION AND DIFFUSION IN ZEOLITE CRYSTALS

ARNE TISELIUS

University of Upsala, Upsala, Sweden

Received June 20, 1935

Zeolites are silicates of calcium, sodium, or potassium together with some aluminum in the anion structure. They occur as minerals in certain volcanic rocks and often form very large and beautiful crystals. Artificial zeolites are made technically for use in water-softening processes, but these substances are not nearly as well defined or well crystallized as the natural minerals.

It has been known for a long time that zeolite crystals show some very unusual properties. (For complete literature references see ref. 2.) They are capable of exchanging reversibly both the cations in the structure against others (for example, Ca against 2Na, and so on), and the water of crystallization against other substances, like ammonia, carbon dioxide, and hydrogen. The cation exchange is the basis of the technical use of zeolites in water-softening. It is quite remarkable that the exchange processes, if performed carefully, leave the crystal lattice unspoiled, as x-ray measurements have shown. Only slight modification of the parameters may occur, corresponding to shrinking or expansion of the lattice. Even the crystal itself may be left entirely intact, transparent, and without cracks. The reverse process gives a crystal which cannot be distinguished from an untreated specimen.

During the last five or ten years our knowledge of the lattice structures of silicates has increased enormously, thanks to the work of W. L. Bragg and his collaborators, especially W. H. Taylor (1). Their studies include a number of the simplest zeolite minerals, and their results give a very good explanation of the remarkable behavior of this class of crystals. For a recent survey of the work on zeolites see the paper by W. H. Taylor (4). It has been found that the zeolite lattice is built up of a very rigid framework of SiO_4 and AlO_4 anions, forming a sort of giant anion. This framework contains channels of sufficiently large diameter to admit cations, water molecules, and other substances of not too big molecular size. The cations and water molecules are not placed at random in the framework, but are fixed to definite positions, which can be determined. The water molecules seem to be most closely associated with the cations of the structure.

The vapor pressure over a dehydrated zeolite crystal, partially saturated

with water, ammonia, or other gas, varies continuously with the amount bound by the crystal. In fact, the curve looks very much like an ordinary adsorption isotherm (see figure 1). There are no sharp discontinuities corresponding to certain molar ratios, as one gets with crystal hydrates and ammoniates.

The study of the adsorption properties of these crystals is of great interest since few, if any, adsorbents possess such a well-defined character. We

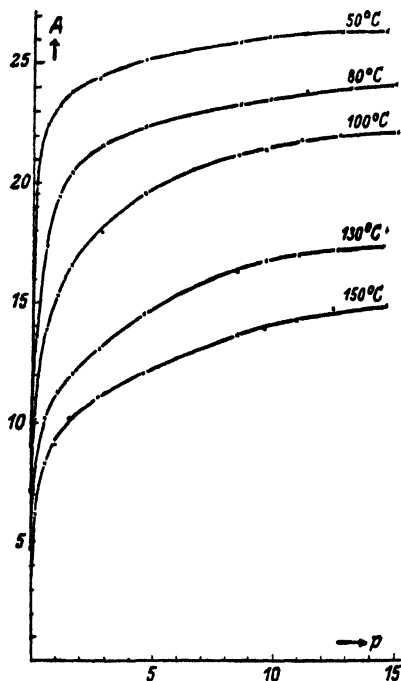


FIG. 1

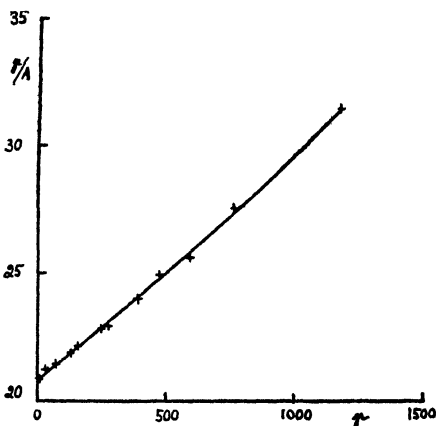


FIG. 2

FIG. 1. Adsorption of water vapor by chabasite (measurements by Tiselius and Brohult). p = pressure in mm. of Hg; A = adsorbed quantity in grams-per 100 grams of dehydrated material.

FIG. 2. Adsorption of ammonia by analcite. p = pressure in mm. of Hg; A = adsorbed quantity in cc. at N.T.P. per gram of dehydrated material.

know that for these adsorbents, the molecules held in the lattice take up definite positions which, in some cases, can be determined. We also know the number of lattice positions available in the crystal. Being silicates, these substances are chemically inert and stable, and therefore give results which are quite reproducible as compared with adsorbents such as charcoal, whose adsorption capacity varies with the origin and previous treatment of the material.

The zeolite structure described above explains an interesting characteristic of zeolite adsorption: there seems to be a certain maximum size of molecules above which no adsorption takes place. Chabasite, for example, adsorbs readily helium, hydrogen, oxygen, nitrogen, carbon dioxide, water, ammonia, methyl alcohol, and ethyl alcohol, but not benzene, ether, the higher alcohols and larger molecules (3, 7). Charcoal, on the other hand, having pores of all sizes, adsorbs very large molecules especially strongly. This may also be a reason for the good reproducibility of zeolite adsorbents: since they admit only quite small molecules which are easily volatilized, they can be freed completely from foreign contaminations by heating in a vacuum.

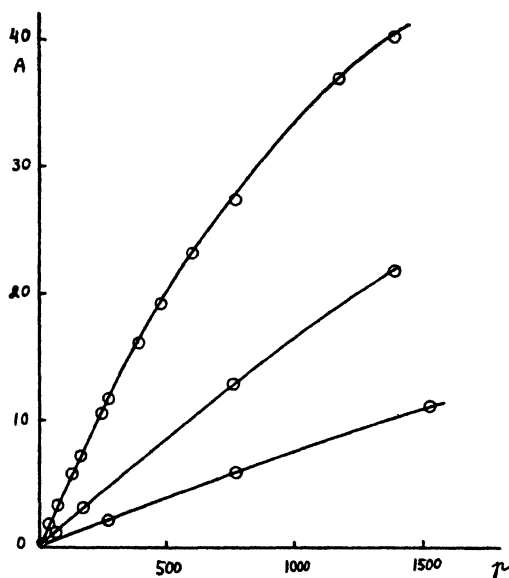


FIG. 3. Adsorption of ammonia by analcite plotted according to Langmuir

Since the molecules in a zeolite lattice are bound to definite positions, one would expect Langmuir's theoretical considerations on adsorption to be applicable. It makes no difference, of course, that we have to deal with a three-dimensional instead of a two-dimensional case. The assumptions made by Langmuir in the simplest cases were that all the adsorbed molecules be bound with the same energy and that there be no interaction between adsorbed molecules. As regards the first point we may obtain some information from x-ray data. W. H. Taylor (4) found that in some cases, for example, thomsonite, there are three different kinds of equivalent positions for the water molecules; in others, for example, scolecite and chavassite (8), there are two kinds; but in two of the cases investigated

hitherto, natrolite and analcite, there is only one kind. Most of the work on zeolite adsorption has been made with chabasite, which is the most convenient to work with experimentally, the adsorption capacity being very high (like that of activated charcoal) and the equilibria being established rapidly.

From the results mentioned, however, analcite and natrolite should be expected to show the simplest behavior. The author has recently measured the adsorption of ammonia on dehydrated analcite, and similar work is being carried on at Upsala by S. Brohult. These measurements are difficult, since the rate of adsorption is low, and it is possible to get equilibria within a reasonable time only at high temperatures (about 250°C.). Some results are shown in figures 2 and 3. The isotherms obey the Langmuir law quite well up to an adsorbed quantity of about 25 cc., as shown by figure 3. Still more important is the fact that the heat of adsorption,

TABLE 1

Heats of adsorption of ammonia on analcite, calculated by use of the Clapeyron equation on the 302°- and the 341.3°-isotherms in figure 2

AMOUNT ADSORBED A CC. PER GRAM OF DEHYDRATED MATERIAL	HEAT OF ADSORPTION Q CALORIES
5	16880
10	16530
15	16860
20	16700
25	16350
Average.....	16640

calculated in the usual way from the isotherms by the Clapeyron equation, is constant over a wide range, as shown by the results given in table 1. This is not usually the case, the heat of adsorption often being much larger for the first amounts adsorbed than for later amounts. It is certainly not true for the system chabasite-water. Still this is a necessary condition for the validity of Langmuir's law. The other condition is the lack of interaction between adsorbed molecules. The deviation of the curve in figure 3 from a straight line for higher concentrations indicates that such an interaction takes place under such conditions, although no determinations of heats of adsorption could be made. The constant a in the Langmuir equation

$$A = \frac{abp}{1 + bp}$$

calculated from the isotherms in figure 2, is 124 cc. at 302°C. and 125 cc. at 341.3°C. The value calculated from the number of spaces available in the

crystal is 118 cc., in good agreement with the experimental value. Usually the constant decreases rapidly with temperature, on account of a wide variation in the energy of adsorption over the surface. As regards the nature of the binding forces in these crystals, the x-ray measurements by W. H. Taylor referred to above (4) show that the water molecules are placed in a more or less deformed tetrahedron, with two sodium ions (for analcite and natrolite) and two oxygen ions at the corners. Evidently the molecule is held in a sort of "dipole hole" and therefore in a strong electrostatic field. This explains why molecules with permanent moments like water and ammonia are so strongly adsorbed. As far as the water molecules are concerned, the arrangement is very similar to that found in ordinary crystal hydrates like $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

The following experiment also indicates that coordination valencies play a rôle. A thin section of a transparent chabasite crystal was completely transformed into copper chabasite by keeping the crystal for several days in a copper sulfate solution at 100°C . The crystal, now showing the characteristic blue color of copper salts, was dehydrated and ammonia let in. An absorption spectrum was taken, using the quartz vacuum chamber described below. This spectrum proved to be identical with that obtained from a solution containing copper ammonium ions.

Zeolites form a very suitable material for investigating the mechanism of the kinetics of adsorption. The rate of adsorption, as measured in the usual way on powders, varies from fractions of one second to almost infinite time. With the same zeolite different substances are adsorbed at very different rates; chabasite takes up hydrogen and water vapor at room temperature in a few minutes, whereas iodine or mercury are taken up at a measurable speed only at temperatures above 100 – 200°C . Different zeolites also differ toward one and the same substance. Analcite does not adsorb any water or ammonia at room temperature, but when heated above 100°C it takes up slowly large amounts of these gases, although the rate becomes sufficiently high to make measurements of equilibria within a reasonable time, only above 250°C . One may obtain some insight into the mechanism of these processes by measurements on powders. Much more detailed information, however, can be obtained by using a direct optical method of observing what happens in a single, evacuated zeolite crystal when a gas, for example, water vapor, is being adsorbed. It has been mentioned already that some zeolite crystals remain transparent after dehydration and readsorption, at least if the operations are performed very slowly and care is taken to avoid too high temperatures or sudden temperature changes. These empty or partially saturated crystals show, when investigated under the polarizing microscope, some very interesting changes in optical properties which can be ascribed to a continuous change of double refraction and extinction angle with the variation of the amount of

water or any other substance in the crystal. Measurements of these quantities can therefore be used as an accurate method of determining the concentration of the adsorbed substance in any part of the crystal and make it possible to observe directly on a single crystal how it is penetrated by a substance being adsorbed.

To make observations of this kind, a small chamber was constructed of optical quartz, fused together vacuum-tight, which could be connected to a vacuum apparatus by a ground joint. The chamber could be placed in a microfurnace under the microscope, and it was thus possible to make observations in a vacuum or any gas pressure desired at temperatures up to about 500°C. The first investigation of this kind was made with the zeolite heulandite, which is especially easy to obtain in optical samples (6). The experimental arrangement is shown in figure 4. K is the quartz

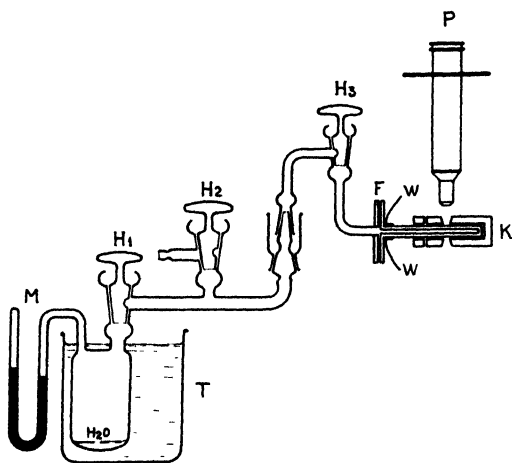


FIG. 4. Experimental arrangement for direct optical observation of diffusion of substances adsorbed in single zeolite crystals.

chamber, enclosed in the microfurnace, P is the polarizing microscope, and the rest is an arrangement for maintaining a constant water vapor pressure. Figure 5 shows a series of exposures of a heulandite crystal adsorbing water. They were taken between crossed nicols in monochromatic (sodium) light. The first exposure shows the partially dehydrated crystal before starting the experiment; the others show the changes taking place after water vapor has been admitted. Two black interference bands, parallel to the surface, migrate slowly into the crystal. In white light a similar series of brightly colored bands is observed. The effect depends, of course, upon the change in double refraction produced by the adsorbed water, the positions of the black bands at any time corresponding to water concentrations giving a double refraction that extinguishes sodium light

for the thickness of the crystal plate employed. More bands are observed (figure 6) if a more strongly dehydrated crystal is used, so that the interval of water concentration becomes greater.

The distance travelled by each band is proportional to the square root of time (figure 7), which is in agreement with the requirements of the theory of diffusion. The measurement of these distances forms a convenient method for determining the diffusion constant, if the relation between double refraction and water concentration in the crystal has been determined. By using a compensator with the microscope one can follow also



FIG. 5



FIG. 6

FIGS. 5 AND 6. Microphotographs of the diffusion of water adsorbed in a heulandite crystal, exposed between crossed nicols in sodium light

the change of double refraction with time at a point a fixed distance from the surface.

These methods reveal a strong anisotropy of diffusion, as figure 8 demonstrates. Furthermore, the diffusion in the direction of observation (perpendicular to the plane of the paper in figures 5, 6, and 8) is immeasurably small.

The results show that the migration of the water molecules in the crystal follows the ordinary diffusion laws for solutions. This is, however, true only for small concentration intervals. Measurements over wider intervals show that Fick's law is still valid, but the diffusion constant is strongly dependent on the concentration, at least for low concentrations, as shown by the results in table 2. The probable reason for this abnormal behavior

is the fact that adsorption is thermodynamically not a case of ideal solution; instead, the vapor pressure increases faster than proportional to the concentration. Moreover, for heulandite, the first amounts of water adsorbed are exceptionally firmly bound by the lattice, making it more difficult for the molecules to jump to an adjacent position. Since we know that the molecules take up definite positions in a lattice, the most plausible mechanism of diffusion is that of "hopping" from one position to another,

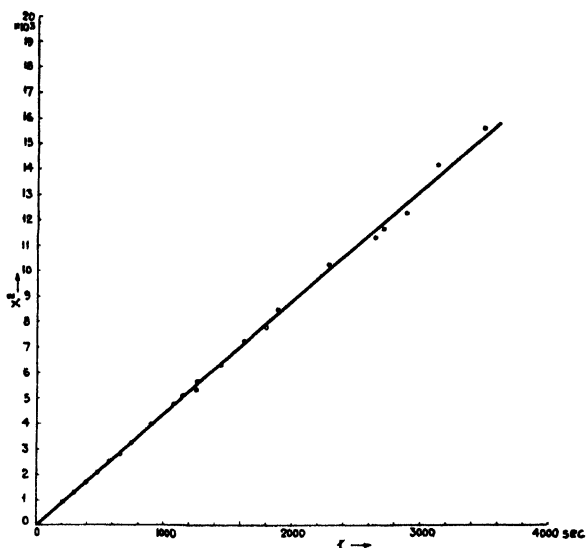


FIG. 7. The square of the travelled distance of each interference band is proportional to t



FIG. 8. Anisotropy of diffusion of adsorbed water in a crystal of heulandite

already assumed by Langmuir and others for describing surface diffusion phenomena. The chance of hopping, and hence the diffusion constant D , should in such a case be proportional to the exponential $e^{-q/RT}$, where q is the energy of activation of diffusion. Plotting $\log D$ against $1/T$ should give a straight line, which is actually the case (figure 9). The different crystallographic directions give different temperature coefficients. For diffusion perpendicular to (201), $q = 5400$ cal.; for diffusion perpendicular to (001), $q = 9140$ cal. It is interesting to compare the values of q thus

obtained with the heat of adsorption, which for water in heulandite is 14,100 cal. at the concentration where the temperature coefficients were determined. For making a diffusion jump, therefore, only 0.4 to 0.65 of the energy required to jump entirely out of the lattice is necessary. One

TABLE 2

Diffusion constants for water in heulandite at 20.0°C., in the direction perpendicular to (201)

WATER CONCENTRATION	$D \times 10^7$	WATER CONCENTRATION	$D \times 10^7$
per cent	cm. ² sec. ⁻¹	per cent	cm. ² sec. ⁻¹
10	about 0.04	15	2.7
11	about 0.2	16	3.6
12	0.7	17	4.0
13	1.3	18	4.0
14	2.0	19	3.3

The diffusion constants in the direction perpendicular to (001) are 11.6 times smaller.

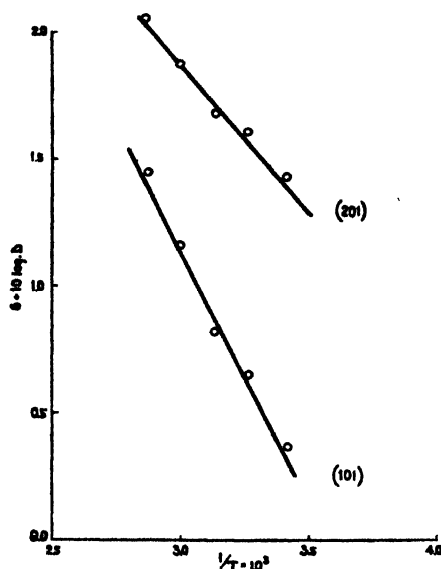


Fig. 9. Temperature dependence of the diffusion constant for water adsorbed in heulandite

may imagine this as a result of the adsorption spaces being so near to each other that their force fields partially overlap.

Recently the author has made similar experiments on the system analcite and ammonia. Although the work has not yet been concluded, it is quite

evident that the diffusion constant is very much lower and the activation energy is very high, equal to or even larger than the heat of adsorption, which in this case is 16,600 cal. One reason for this may be that the adsorption spaces in analcite are very widely separated (as is known from its crystal structure and water content).

The kinetics of adsorption, especially the slow or activated adsorption, has attracted much attention during recent years. The experiments have so far been made exclusively on powders or conglomerates of crystals by volumetric methods. However, in the investigations just described it is certain that the diffusion in the crystal is the rate-determining factor. This is evident from the fact that the concentration at the surface all the time during the adsorption process is constant and equal to the saturation value, as can be observed directly under the microscope. This may not always be the case for adsorption in zeolites, and it is therefore valuable to be able to get additional information by the optical method described.

REFERENCES

- (1) BRAGG, W. L.: *The Structure of Silicates*, 2nd edition (1932).
- (2) HEY, M. H.: *Mineralog. Mag.* **23**, 422 (1930).
- (3) SCHMIDT, O.: *Z. physik. Chem.* **133**, 263 (1928).
- (4) TAYLOR, W. H.: *Proc. Roy. Soc. London* **145A**, 80 (1934).
- (5) TISELIUS, A., AND BROHULT, S.: *Z. physik. Chem.* **168A**, 248 (1934).
- (6) TISELIUS, A.: *Z. physik. Chem.* **169A**, 425 (1934).
- (7) WEIGEL, O., AND STEINHOFF, E.: *Z. Krist.* **61**, 125 (1924).
- (8) WYART, J.: *Dissertation*, Paris, 1933, p. 48.

THE SORPTION OF BROMINE AND IODINE BY ACTIVATED CHARCOAL

L. H. REYERSON AND A. E. CAMERON

School of Chemistry, University of Minnesota, Minneapolis, Minnesota

Received August 2, 1935

In a previous publication (1) a method was described which made it possible to study the sorption of bromine and iodine by porous adsorbents over a rather wide pressure range at several temperatures. At that time the sorption of bromine and iodine by silica gel at several temperatures was reported. Equilibria for adsorption and desorption were established rapidly in the case of silica gel. In the present study on charcoal equilibrium was reached slowly, so that rates of sorption were measured in addition to the determination of the amounts taken up at equilibrium.

The charcoal used in this investigation was prepared from coconut shells. Broken coconut shells were cleaned and then placed in a large Soxhlet extractor where they were successively extracted for prolonged periods with ether, alcohol, and finally water. The extracted shells were coked in a covered iron crucible in a sand bath. The temperature was raised slowly to 550–575°C. and held there for half an hour after the last flammable vapors came off. After cooling the charcoal was crushed and sieved. A portion of 25 g. that passed a 10-mesh and was retained by a 20-mesh sieve was taken for activation. This was packed in a clean silica combustion tube and heated to 850°C. in an electric furnace. Superheated steam from a small boiler was passed over the charcoal for thirty minutes. After cooling, the average loss in weight on activation by steam was found to be 25 per cent of the initial weight. The steam-activated charcoal was then placed in a silica tube and heated to 700°C. while it was evacuated with a pair of Langmuir condensation pumps. The charcoal was protected from mercury vapor by a liquid air trap. After a 24-hour evacuation the charcoal was cooled to room temperature and oxygen admitted. After standing some time in an atmosphere of oxygen the charcoal was again heated and evacuated for a period of 48 hours. The charcoal was then cooled in an atmosphere of nitrogen. On ashing in a platinum crucible the following results were obtained: ash, 0.185 per cent; ash as sulfate, 0.233 per cent; silica, 0.026 per cent.

The charcoal was crushed in an agate mortar and that portion used which passed a 60-mesh and was retained by a 100-mesh screen. About 0.2 g.

TABLE 1
Sorption of bromine by charcoal

PRESSURE IN MM. CORRECTED	X/M MILLIMOLES PER GRAM OF SORBENT	HOURS FOR READING	PRESSURE IN MM. CORRECTED	X/M MILLIMOLES PER GRAM OF SORBENT	HOURS FOR READING
Isotherm at 58.0°C.			Isotherm at 98.1°C.—concluded		
0.63†	4.155	9.0	266.2	5.335*	22.0
3.0†	4.607	4.5	68.9	5.076*	22.0
11.4†	4.972	14.0	18.2	4.776*	25.0
68.8	5.358	20.0	3.0†	4.124*	10.0‡
140.4	5.554	21.5	0.03†	3.121*	22.0
265.7	5.665	23.0	Isotherm at 137.6°C.		
473.0	5.779	24.0	0.03†	2.611	20.5
691.8	5.849	22.0	1.8†	3.355	23.5
474.1	5.804*	22.0	19.2	4.207	24.0
265.8	5.702*	14.0	68.1	4.629	19.0
140.4	5.579*	25.0	265.8	4.990	23.0
67.4	5.459*	27.0	791.5	5.217	24.0
11.4†	5.149*	10.5	266.7	5.013*	24.0
1.8†	4.787*	13.0	69.5	4.671*	32.0
0.63†	4.445*	16.0	20.3	4.244*	21.0
0.03†	3.904*	35.0	1.8	3.377*	25.5
Check isotherm at 58.0°C. after deter- mining isotherms at higher temper- atures recorded in this same table			0.03	2.623*	24.5
			Isotherm at 178.4°C.		
0.03†	3.431	72.0	0.03†	2.250	38.0
70.6	5.456	23.5	3.0	3.016	33.0
695.6	5.836	24.0	16.8	3.619	25.0
68.3	5.456*	25.0	67.2	4.143	20.0
0.00‡	3.163*	24.0	266.8	4.628	23.5
Isotherm at 98.1°C.			787.8	4.899	26.0
0.03†	3.044	22.0	266.7	4.645*	20.0
3.0†	4.088	24.0	69.2	4.186*	27.0
18.6	4.729	27.0	17.8	3.652*	26.5
68.3	5.048	24.0	3.0†	3.054*	23.5
266.2	5.311	21.0	0.03†	2.247*	72.0
792.3	5.527	29.0			

* Desorption readings.

† Values derived from vapor pressure function.

‡ High vacuum with charcoal at 58.0°C.

§ Thermostat had to be reset on temperature.

TABLE 2

Rates of sorption of bromine by charcoal at 137.6°C.

TIME IN MINUTES	SPRING LENGTH IN MM.	MILLI-MOLES PER GRAM	TIME IN MINUTES	SPRING LENGTH IN MM.	MILLI-MOLES PER GRAM	TIME IN MINUTES	SPRING LENGTH IN MM.	MILLI-MOLES PER GRAM
Pressure = 0.03 mm.*; temperature = 98.1°C. 137.7°C.			Pressure = 265.8 mm.			Pressure = 20.3 mm.*		
0	60.031	3.120	0	62.443	4.623	0	62.504	4.671
20	59.597	2.956	5	62.950	4.906	15	61.900	4.313
65	59.252	2.755	10	62.985	4.932	25	61.877	4.293
195	59.125	2.678	25	62.999	4.946	85	61.824	4.271
990	59.009	2.600	180	63.037	4.974	195	61.796	4.255
1230	59.001	2.587	400	63.040	4.976	1070	61.780	4.242
			730	63.055	4.985	1280	61.779	4.241
			1390	63.064	4.990			
Pressure = 1.8 mm.			Pressure = 791.5 mm.			Pressure = 1.8 mm.*		
0	59.001	2.587	0	63.064	4.990	0	61.779	4.241
20	59.829	3.086	5	63.370	5.153	10	61.110	3.851
45	60.043	3.220	10	63.396	5.179	20	60.831	3.687
240	60.221	3.304	30	63.405	5.184	30	60.688	3.597
430	60.249	3.339	170	63.420	5.193	55	60.532	3.511
1260	60.276	3.361	410	63.433	5.201	420	60.361	3.411
1355	60.267	3.355	830	63.448	5.216	1090	60.328	3.391
			1420	63.450	5.217	1600	60.302	3.376
Pressure = 19.2 mm.			Pressure = 266.7 mm.*			Pressure = 0.03 mm.*		
0	60.267	3.355	0	63.450	5.217	0	60.302	3.376
15	61.289	3.951	5	63.166	5.050	5	60.234	3.324
20	61.457	4.073	15	63.146	5.038	10	60.082	3.241
25	61.491	4.069	60	63.111	5.018	20	59.901	3.122
40	61.564	4.112	270	63.107	5.015	60	59.518	2.909
100	61.633	4.146	520	63.103	5.013	120	59.340	2.807
645	61.703	4.176	760	63.104	5.014	195	59.222	2.720
1425	61.715	4.174	1330	63.102	5.012	250	59.184	2.713
						910	59.110	2.657
Pressure = 68.1 mm.			Pressure = 69.5 mm.*			1460	59.021	2.617
0	61.715	4.174	0	63.102	5.012			
5	62.034	4.370	5	62.656	4.757			
10	62.303	4.529	15	62.620	4.739			
15	62.357	4.566	60	62.540	4.692			
30	62.370	4.586	520	62.520	4.680			
60	62.395	4.607	670	62.517	4.678			
140	62.413	4.612	885	62.516	4.678			
245	62.415	4.613	1935	62.504	4.671			
495	62.425	4.619						
1100	62.443	4.623						

* Desorption readings.

of this charcoal was weighed into the little glass bucket of the McBain balance. The experimental procedure was the same as previously described (1).

Table 1 gives the results obtained for the sorption of bromine by charcoal at 58°, 98.1°, 137.6°, and 178.4°C. Table 2 gives the complete data at 137.6°C. for the rates of adsorption and desorption of bromine by the charcoal. Table 3 records the results of the sorption studies of iodine on charcoal. It should be noted that during desorption it was never possible to

TABLE 3
Sorption of iodine by charcoal

PRESSURE IN MM. CORRECTED	X/M MILLIMOLES PER GRAM OF SORBENT	HOURS FOR READING	PRESSURE IN MM. CORRECTED	X/M MILLIMOLES PER GRAM OF SORBENT	HOURS FOR READING
Isotherm at 178.4°C.			Isotherm at 218.8°C.—concluded		
0.03†	0.07492	5.5	234.0	0.2721	2.2
10.6	0.2341	2.0	423.5	0.2829	2.2
80.0	0.2774	12.5	560.0	0.2882	2.7
169.0	0.2897	3.0	317.5	0.2784*	2.2
234.0	0.2963	1.5	100.0	0.2593*	11.0
368.0	0.3036	1.2	26.0	0.2315*	5.0
100.0	0.2815*	4.0	2.0†	0.1470*	6.0
26.0	0.2614*	10.5	0.03†	0.0539*	22.0
4.3	0.2205*	2.5	0.00‡	0.0073*	8.0
0.03†	0.0759*	30.0	Isotherm at 178.4°C.		
Isotherm at 218.8°C.			2.0†	0.2064	1.0
0.03†	0.0416	17.0	79.7	0.2889	18.0
10.6	0.1881	3.5	168.4	0.3011	3.0
80.0	0.2525	1.2	420.0	0.3175	2.0
169.0	0.2671	12.0	315.5	0.3141*	14.0
			118.5	0.2963*	4.0

* Desorption readings.

† Value derived from vapor pressure function.

‡ High vacuum at 525°C., spring measured at 37°C.

completely remove the bromine or iodine which had been adsorbed by the activated charcoal.

In a previous paper in this journal (2) figures were given for the data here presented. They are not therefore repeated here. The data are given as a matter of record for other investigators.

SUMMARY

1. Data are given for the sorption of bromine by activated charcoal at 58°, 98.1°, 137.6°, and 178.4°C.

2. Data are given for the rates of adsorption and desorption of bromine by charcoal at 137.6°C.

3. Data are given for the sorption of iodine by activated charcoal at 178.4° and 218.8°C.

REFERENCES

- (1) CAMERON, A. E., AND REYERSON, L. H.: J. Phys. Chem. **39**, 169 (1935).
- (2) REYERSON, L. H., AND CAMERON, A. E.: J. Phys. Chem. **39**, 181 (1935).

STUDIES OF POLARIZATION DISCHARGES IN MULTIPLE ELECTRODE SYSTEMS

HERSCHEL HUNT, JOSEPH F. CHITTUM, AND HENRY M. GRUBB¹

Department of Chemistry, Purdue University, West Lafayette, Indiana

Received May 23, 1955

Each of two identical exploring electrodes, in equilibrium with an electrolytic solution, immersed between the current electrodes of an electrolytic cell, will conduct approximately the same amount of current. The current passing through two such exploring electrodes in the same direction will build up a positive pole and an equal negative pole on each electrode. The two exploring electrodes will form two concentration polarization storage batteries that will rapidly discharge when the polarizing current is stopped because each battery is shorted by the metal of the electrode. A definite current will continue to flow through the solution between the two exploring electrodes, if one tries to measure the potential difference between the two electrodes immediately after the applied current is stopped. Under these circumstances, we have observed currents that last for minutes and have measured these currents in various electrodes and cell systems.

The current electrodes become polarized during the passage of current. Also it has been pointed out that each current electrode becomes polarized differently at different points on its surface. We have observed currents that last for minutes midway between two electrodes twenty inches apart, when the only possible source of these currents was the two polarized current electrodes behaving as two shorted storage batteries connected together. There was no metallic connection between these electrodes, only the electrolytic connection.

Since the effect shows up with alternating current also, such currents will obviously affect the measurement of the conductivity and dielectric constant of electrolytes if electrodes are used. Therefore, the second part of this study was made to investigate the source of these currents and, if possible, their magnitude under various conditions. The variables cannot all be accurately controlled and the currents measured cannot be used to correct existing data, but it is pointed out that in the future apparatus should be designed that will eliminate any possibility of having these

¹ Purdue Research Foundation Fellow.

currents when they are important. The experimental part will indicate that the latter precaution is imperative.

EXPERIMENTAL

Electrodes and cells

Calomel, hydrogen, mercury-mercuric oxide, mercury-mercurous sulfate, silver, silver-silver chloride, and copper electrodes, all prepared by standard procedures, were used with solutions that would be in equilibrium with the electrodes. The most satisfactory chloride electrodes were made by uniformly coating pure silver wire or silver foil with the chloride, by electrolysis in a concentrated solution of the chloride to be studied. Electrodes whose potentials varied by less than a tenth of a millivolt could be prepared by this method. Two shapes were used, straight wires (size 16) with about two inches immersed vertically in the solution, as in figure 1, and electrodes with the same amount of surface exposed, but

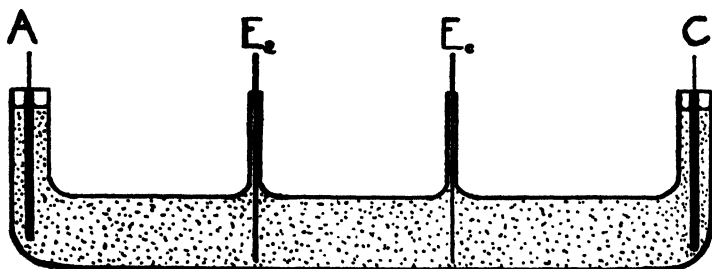


FIG. 1. The simple cell. A, anode; C, cathode; E_a and E_c , exploring electrodes

bent as in figure 2. The current electrodes, prepared in the same way, are designated as A and C; the exploring electrodes as E_a and E_c .

Measuring instruments

A Leeds and Northrup galvanometer (Type HS) of 2×10^{-8} amperes per millimeter current sensitivity and of very low resistance was used to measure the current. A vacuum tube voltmeter (Tube No. 30), with high resistance, was used for a part of the measurements.

Switch

A double, double pole, single throw switch on Bakelite with platinum to mercury contacts was employed. It was capable of breaking both sides of the charging current and connecting the measuring instrument 0.001 of a second later. A walking beam was attached to the switch to manipulate the protecting glass shield (I in figure 2).

Procedure

The experimental procedure involved the arbitrary control of the time the applied current was allowed to flow, the magnitude of the current, the resistance of the solution between the exploring electrodes, the frequency of the current if alternating current is used, the size and shape of the exploring electrodes, the solvent, the solute, the size and shape of the vessel containing the electrodes, the time elapsing between cutting off the applied current and measuring the produced current, the position of E_a and E_c with respect to A and C, and the temperature of the solution. The

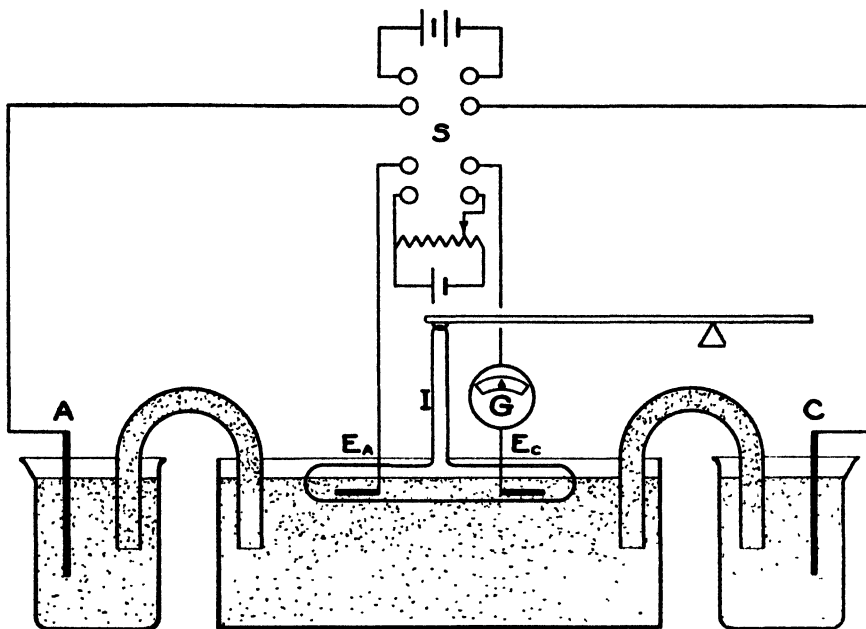


FIG. 2. The complete cell

time of passage of current through the solution was taken as thirty seconds. An average effect independent of imperfections in construction was obtained by reversing the current.

During experiments of the first type, the apparatus shown in figure 2 was used with some one of the above mentioned solution-electrode systems. The switch was thrown after thirty seconds, thereby disconnecting the applied current, lowering the shield from around E_a and E_c in order to expose them to the solution through which a current had passed, and connecting the measuring apparatus. No current was detected in the solution between E_a and E_c .

In the second type of experiment the same procedure, without the glass shield, was followed. Then a current of 1×10^{-4} to 1×10^{-2} milliamperes was found flowing through the measuring instruments; the current was flowing in the same direction in which it would flow if the instruments were connected while the applied current was flowing.

In the third type of experiment the current electrodes were placed inside the trough, about six inches outside E_a and E_c , which were four inches apart. The glass shield protecting E_a and E_c from the charging current was replaced, the solution was violently stirred, and the regular procedure was repeated to stop the current and to expose E_a and E_c . (a) If the current electrodes were placed vertically in the cell, a current of 1×10^{-5} to 1×10^{-2} milliamperes was found flowing through the instruments in the same direction as in the previous experiment (figure 4). (b) If the current electrodes were placed horizontally in the cell, a similar current was found flowing in the opposite direction (figure 5).

The fourth type of experiment was a repetition of the third, except that the shield was not used, and the current electrodes were polarized in a beaker completely outside of the system, washed in distilled water, and then transferred to the cell (figure 2). The presence of the polarized electrode produced a current of 1×10^{-3} milliamperes in the measuring instruments in the same directions as in the third type of experiments, which means that the polarization is in the surface of the electrodes and is not uniform over the surface of the same electrode.

The above group of experiments gives us some definite information concerning the nature of the phenomena. The observed current has nothing to do with general concentration polarization of the electrolyte. It is not a phenomenon of some peculiar dielectric polarization, nor an external condenser in the electrical system.

In the fifth type of experiment the current electrodes A and C were returned to the beakers, and the electrodes E_a and E_c were rotated at a high rate of speed (more than 100 R.P.M.). The results were very similar to the results obtained in the second type of experiment, except that the currents measured were much smaller than when the electrodes E_a and E_c were stationary. If only one electrode was rotated, we obtained electrokinetic phenomena about which we will report later.

The above experiment seemed difficult to interpret except in the light of the fact that the phenomenon exists even though the direction of the applied current through E_a and E_c may be reversed rapidly. In the sixth type of experiment E_a and E_c were left exposed to alternating currents of frequency varying from 20 to 12,000 cycles per second (General Radio beat frequency oscillator). Again there was a current flowing after the applied current was stopped, which varied in sign and magnitude. The maximum effect using the alternating current appeared to have a peak

value at about 200 cycles per second, but definitely existed at as high a frequency as 12,000 cycles. The effect was 1×10^{-3} milliamperes and greater between the electrodes of a conductivity cell (Washburn, Type A, electrodes platinized) in dilute solutions, using a 500-cycle applied current.

In experiments of type seven, either A or C was a circular electrode, and the other electrode was placed at its center. If E_a and E_c were somewhere in between these electrodes a small effect was obtained. If E_a and E_c were outside a large effect was obtained, a current of 1 milliampere or more, the direction of which can be reversed by rotating the circular electrode through 180° . These results, with E_a and E_c outside, were not obtained if the circular electrode was a metal cylinder that contained no electrolytic connection between the solution inside and the solution outside of it. One small electrolytic connection, 1 mm. in diameter or less, was sufficient.

The results of these last experiments are supplementary evidence that an electrode is polarized by a current passing across the interface but a small fraction of a second. Alternating the current does not periodically restore the original situation, but increases the sharpness of the differential polarization. Unfortunately, the authors are not able to reproduce their data quantitatively on account of the difficulty of controlling all the variables. Therefore they do not feel that the actual figures need be published. However, they can point out a number of the variables and their influence on the current.

The apparatus and procedure being the same (the current electrodes not interfering), the magnitude of the effect, as indicated by the current in the measuring instruments, increases with the following: an increase in the current through the cell, an increase of the resistance of the electrolyte, an increase in the ratio of the resistances of the possible current paths, an increase in the viscosity and decrease of the dielectric constant of the solvent, an increase in size, especially the length, of the electrodes E_a and E_c that are responsible for the effect; it also increases the greater the difference in potential between any two points on the polarized electrodes. The effect decreases with an increase in the resistance of the measuring instrument, an increase in the temperature, and withdrawal of the exploring electrodes into side tubes out of the current path, as is possible in the apparatus of figure 1. When the current electrodes are capable of giving their effect also, the effect is quite dependent on the size and shape of these electrodes, but it is independent of the rate of stirring of the electrolyte up to the limit of stirring with a rod. Care is used to make sure that E_a and E_c , if straight wires, are always parallel to each other and perpendicular to the central lines of force between A and C, otherwise a double effect with opposite signs may be observed. Two positive and two negative currents have been observed with one period of polarization. The

depth of the solution in the cell of figure 2 permits currents to flow that are not detectable in the cell shown in figure 1. We are only able to measure the resultant current in each case, and not even it at its maximum value, since the effect decays very rapidly at first.

DISCUSSION OF RESULTS

In order to explain all of the phenomena they must be treated as being made up of two effects: firstly, an effect due to the polarization at the ends of the exploring electrodes, E_a and E_c ; secondly, an effect due to the differential polarization of each of the current electrodes at different points on their surface. The current measured in the first case is illustrated in figure 3 as the resultant of four currents, 1, 1', 2, and 3 caused by the polarization of E_a and E_c . If no metallic connection is made between E_a and E_c , then currents 1, 1', and a modified form of 2 will discharge the

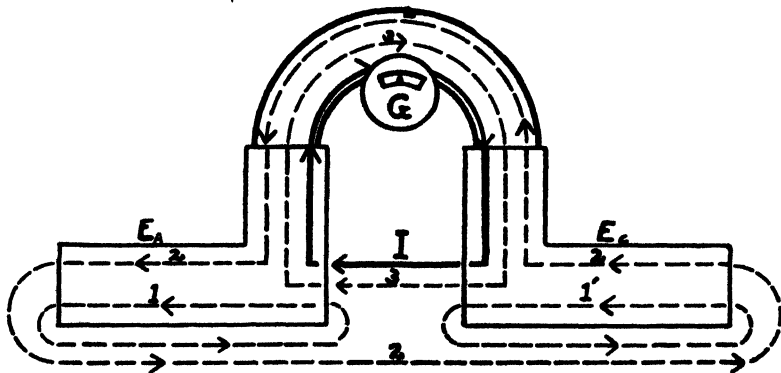


FIG. 3. Discharge circuits

polarization. Current 2, in this case, would flow in both directions through the solution from E_c to E_a . If the galvanometer connects the two electrodes we have currents 2 and 3. Current 2 will not be equal to 3 unless the resistances in the two circuits are the same, and they obviously are not. This action of the currents sets up a resultant current in the galvanometer in the direction indicated by I. Experiments of the first and second type without exception bear out this mechanism.

When the exploring electrodes are protected while the current passes, and only the effects of the current electrodes are obtained, the path of the effective current is shown for each of the typical cases in figures 4 and 5. In the case of the horizontal electrodes the point of maximum polarization is at the end of the current electrodes. On discharge, the current follows the path indicated in figure 5. In the case of the vertical electrodes the point of maximum polarization is at the bottom of the electrodes (1). On discharge the current follows the path indicated in figure 4. The

experiments of the third and fourth type without exception substantiate the above mechanism.

These experiments are of value in that they demonstrate some very simple principles in systems where there has been a tendency to overlook their significance. They demonstrate (1) that a resultant current is produced in a solution between two shorted batteries dipping into the same solution, if the electrical lines of force are not symmetrical and if metallic connection is made between the shorted batteries; (2) that a polarized electrode must be treated as a number of spot electrodes of widely varying polarization potentials, i.e., it is at least one shorted battery; (3) that the use of alternating current for polarizing the electrodes

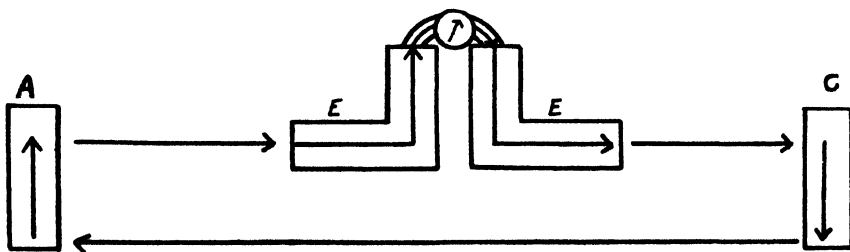


FIG. 4. Discharge circuit

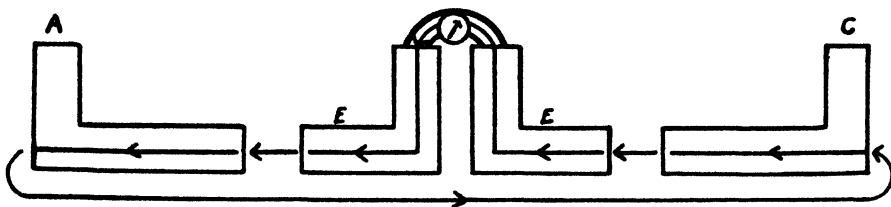


FIG. 5. Discharge circuit

does not change the situation, probably because the current in the two directions crosses the electrode interface at different points; and (4) that the polarization potential of an electrode measured in any of the usual ways gives some sort of a weighted average of all of the polarization potentials.

SUMMARY

Currents in an electrolytic solution that are produced by the presence of polarized electrodes have been discussed. The importance of considering them when dealing with electrolytic phenomena has been pointed out.

REFERENCE

- (1) FERGUSON AND DUBERNELL: *Trans. Electrochem. Soc.* **63**, 221 (1933).

THE OXIDATION POTENTIAL OF THE SYSTEM POTASSIUM MOLYBDOCYANIDE-POTASSIUM MOLYBDICYANIDE, AND THE EFFECT OF NEUTRAL SALTS ON THE POTENTIAL

I. M. KOLTHOFF

School of Chemistry, University of Minnesota, Minneapolis, Minnesota

AND

WM. J. TOMSICEK

Department of Chemistry, College of St. Thomas, St. Paul, Minnesota

Received June 20, 1935

Collenberg (1) determined the oxidation-reduction potentials of molybdocyanide and molybdicyanide solutions. His measurements, however, were made in the presence of potassium chloride, the concentration of which was not known. In the preparation of his solution of potassium molybdicyanide an excess of potassium chloride was used to decompose precipitated silver molybdicyanide in order to form the soluble potassium molybdicyanide and insoluble silver chloride. His data do not allow an extrapolation of the potential to an ionic strength of zero. For this reason we have determined the oxidation-reduction potentials at increasing dilutions in order to find the potential at an ionic strength of zero. In addition the effects of neutral salts on the potential were studied.

MATERIALS USED

Potassium molybdocyanide

This product was prepared according to the method of Olsson (5) and recrystallized three times from water by the addition of ethyl alcohol. The water content of the air-dried product was determined by heating in the electric oven at a temperature of 105°C. for five hours. The loss in weight from two samples gave 1.993 and 2.006 moles of water, respectively. Two other samples were titrated at the same acidity as in the potentiometric method described below, with a permanganate solution standardized against Kahlbaum's sodium oxalate, and the results agreed with the formula $K_4Mo(CN)_6 \cdot 2H_2O$ within 0.5 per cent. Erio-grün was used as an indicator in the permanganate titration, since the golden-yellow color of the potassium molybdicyanide formed masks the permanganate endpoint. The volume of permanganate used to obtain the endpoint with erio-grün was found to be identical with that found in the potentiometric method.

In figure 1 the change in potential is given in the potentiometric titration of a mixture of 100 ml. of 0.007 molar molybdocyanide and 2 ml. of concentrated sulfuric acid with 0.1 normal permanganate, the saturated calomel electrode being used as the reference electrode.

Aqueous solutions of potassium molybdocyanide are relatively stable, as shown by the fact that the titer was constant for at least two days. In our work fresh solutions were prepared every second day.

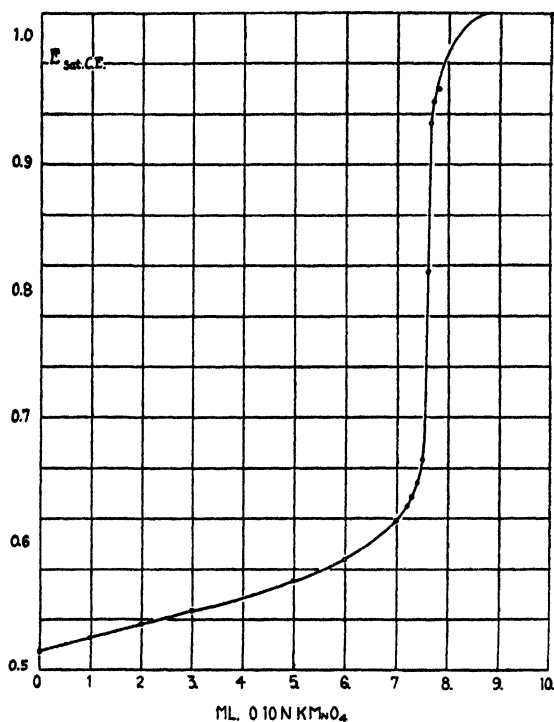


FIG. 1. Titration curve for $\text{K}_4\text{Mo}(\text{CN})_6$.

Potassium molybdicyanide

Solutions of potassium molybdocyanide, acidified with sulfuric acid, were oxidized with potassium permanganate until a pink color persisted. An excess of silver nitrate was then added to precipitate silver molybdicyanide. The precipitate was filtered off on a Buchner funnel and washed until no test for the silver ion was obtained in the washings. The moist silver molybdicyanide was suspended in water and shaken with somewhat less than the equivalent quantity of potassium chloride, leaving some silver molybdicyanide undecomposed. The filtered solution was used as a stock solution, its concentration being determined by electrometric titration with a standard solution of potassium ferrocyanide.

Fieser (2) used the same procedure for the determination, but does not state the conditions for the titration. We found good results in neutral or weakly alkaline medium, but no distinct jump was observed in acid medium. This is easily explained by the fact that the oxidation potential of the ferrocyanide-ferricyanide system increases much more with increasing hydrogen-ion concentration than that of the molybdocyane-molybdicyanide system. Figure 2 shows the change of potential in the

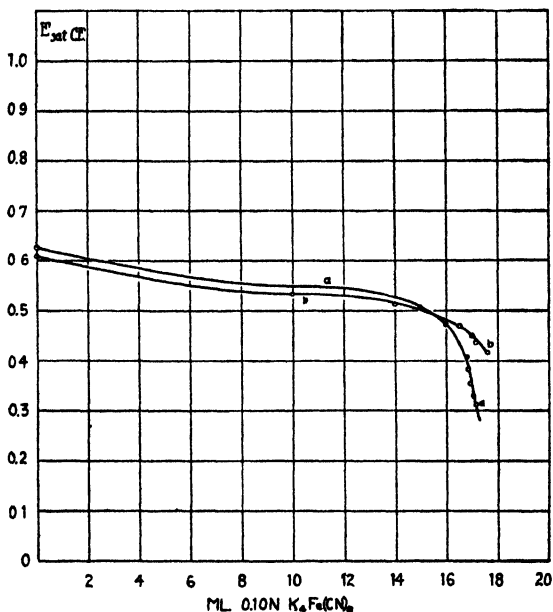


FIG. 2. Titration curve for $K_2Mo(CN)_8$. a = neutral medium; b = acid medium

TABLE 1

Decrease in strength of potassium molybdicyanide in per cent after six days

ACID SOLUTIONS		NEUTRAL SOLUTIONS		BASIC SOLUTIONS	
Diffuse light	Dark	Diffuse light	Dark	Diffuse light	Dark
19.3	1 3	23 4	2 2	29 3	3.3

titration of 100 ml. of 0.016 molar molybdicyanide with potassium ferrocyanide in the presence of 1 ml. of concentrated sulfuric acid and in neutral medium.

Solutions of potassium molybdicyanide were found to be extremely sensitive to light. A 0.016 molar solution analyzed in the dark and then placed in the window in direct sunlight was found to change in titer by 22 per cent in two hours. Solutions kept in the dark changed approximately

1 per cent in six days. Hydrogen ions have a stabilizing influence on solutions of potassium molybdicyanide. The effects of acetic acid and sodium carbonate on the decomposition of potassium molybdicyanide are shown in table 1. The light to which the solutions were exposed was diffuse sunlight in a north room of the laboratory.

TABLE 2

Oxidation-reduction potentials of potassium molybdocyanide-potassium molybdicyanide solutions at 25°C.

$K_2Mo(CN)_6$	$K_2Mo(CN)_6$	RATIO MOLYBDI MOLYBDO	TOTAL μ	$\sqrt{\mu}$	$E_{Q.H.}$	$E_{N.H.E.}$	e_0
<i>M</i>	<i>M</i>						
0.03012	0.02888	1.0430	0.4695	0.6852	0.2155	0.7919	0.7908
0.003012	0.002888	1.0430	0.04695	0.2167	0.1800	0.7564	0.7553
0.001205	0.001155	1.0430	0.01878	0.1371	0.1697	0.7461	0.7450
0.000602	0.000577	1.0430	0.00938	0.0968	0.1638	0.7402	0.7391
0.02696	0.02872	0.9390	0.44896	0.6701	0.2131	0.7895	0.7911
0.00539	0.00574	0.9390	0.08974	0.2996	0.1870	0.7634	0.7650
0.002696	0.002872	0.9390	0.04489	0.2119	0.1776	0.7540	0.7556
0.001080	0.001150	0.9390	0.01798	0.1341	0.1675	0.7439	0.7455
0.00054	0.000574	0.9390	0.00898	0.0950	0.1615	0.7379	0.7395
0.000270	0.000287	0.9390	0.00449	0.0670	0.1577	0.7341	0.7357
0.000108	0.000115	0.9390	0.00180	0.0424	0.1553	0.7317	0.7333
0.02112	0.03044	0.6940	0.43212	0.6574	0.2045	0.7809	0.7903
0.00422	0.006088	0.6940	0.08622	0.2936	0.1786	0.7550	0.7644
0.00211	0.003044	0.6940	0.04311	0.2076	0.1688	0.7452	0.7546
0.00084	0.001218	0.6940	0.01725	0.1313	0.1585	0.7349	0.7443
0.000422	0.000609	0.6940	0.00862	0.09285	0.1526	0.7290	0.7384
0.000211	0.000304	0.6940	0.00431	0.06566	0.1485	0.7249	0.7343

e_0 refers to the potential of an equimolecular solution of molybdocyanide and molybdicyanide calculated from the figures in columns 3 and 7.

$E_{Q.H.}$ is the E.M.F. as measured against the quinhydrone electrode in a solution being 0.01 *N* in hydrochloric acid and 0.09 *N* in potassium chloride.

$E_{N.H.E.}$ is the E.M.F. referred to the normal hydrogen electrode as calculated from $E_{Q.H.}$ (see ref. 4).

EXPERIMENTAL PROCEDURE

To a solution of potassium molybdicyanide, prepared as described above, was added a weighed quantity of potassium molybdocyanide. The solution was then analyzed for molybdocyanide and molybdicyanide by titration with potassium permanganate and potassium ferrocyanide, respectively, and used as a stock solution for the dilution measurements. All flasks and apparatus used to contain the solutions were coated with black lacquer and kept in the dark. The measurements were made in a darkened room. For details regarding the experimental technique reference is

made to a previous paper (3). Table 2 gives the results of measurements of various dilutions of three stock solutions containing different ratios of molybdocyanide and molybdicyanide. By "Total μ " is meant the sum of the ionic strengths of molybdocyanide and molybdicyanide.

The values of ϵ'_0 found in table 2 were plotted against $\sqrt{\mu}$ on large cross section paper and extrapolated to determine the value of the normal potential at zero ionic strength. The extrapolated value was found to be 0.7260 volt, referred to the normal hydrogen electrode. The curve is shown in

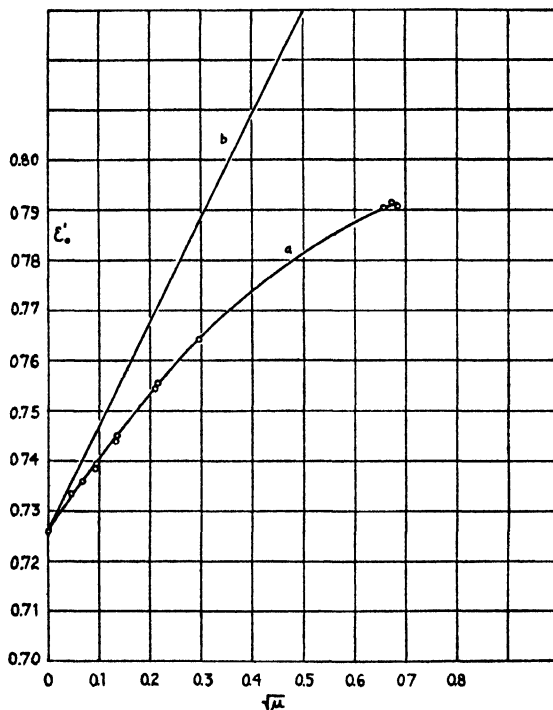


FIG. 3. Change of normal potential ϵ'_0 with increasing ionic strength μ . a = experimental data (table 2); b = calculated values

figure 3. The straight line in the figure represents the values of ϵ'_0 calculated on the basis of the limiting Debye-Hückel equation:

$$\epsilon'_{0 \text{ calculated}} = \epsilon_0 + 0.0591 \log \frac{c_{\text{MoCn}_5} \cdots}{c_{\text{MoCn}_6} \cdots} \cdot \frac{f_3}{f_4} \text{ (at } 25^\circ\text{C.)}$$

where $\epsilon_0 = 0.7260$ volt, and f_3 and f_4 are the activity coefficients of the molybdicyanide and molybdocyanide, respectively.

Since ϵ'_0 refers to the value for equimolecular concentrations of molyb-

dicyanide and molybdicyanide, then the calculated value of ϵ'_0 is

$$\epsilon'_0 = \epsilon_0 + 0.0591 \log \frac{f_3}{f_4}$$

in which, according to the limiting Debye-Hückel expression, $\log \frac{f_3}{f_4} = 3.5 \sqrt{\mu}$.

TABLE 3

Log $\frac{f_3}{f_4}$ in dilute solutions of molybdo-molybdicyanides in the presence of various electrolytes

μ	$\sqrt{\mu}$	$\log \frac{f_3}{f_4}$	μ	$\sqrt{\mu}$	$\log \frac{f_3}{f_4}$
KCl			HCl		
0.01	0.1365	0.4068	0.0104	0.1380	0.3796
0.025	0.1833	0.5695	0.0522	0.2466	0.6305
0.05	0.2421	0.7322	0.10	0.3296	0.7779
0.1	0.3295	0.9118			
0.25	0.5080	1.1950			
0.5	0.7132	1.4373			
NaCl			NH ₄ Cl		
0.01	0.1317	0.3756	0.0107	0.1343	0.4136
0.025	0.1797	0.5166	0.0269	0.1850	0.5813
0.10	0.3276	0.8288	0.1075	0.3390	0.9237
0.5	0.7123	1.3254	0.5374	0.7448	1.4525
LiCl			CaCl ₂		
0.01	0.1317	0.3813	0.01	0.1317	0.6100
0.025	0.1797	0.5085	0.025	0.1797	0.8050
0.1	0.3276	0.8085	0.1	0.3276	1.1322
0.25	0.5073	1.0593	0.5	0.7123	1.5340
SrCl ₂			BaCl ₂		
0.01	0.1317	0.6186	0.01	0.1317	0.6610
0.025	0.1797	0.8390	0.025	0.1797	0.8813
0.1	0.3276	1.1814	0.1	0.3276	1.2203
0.5	0.7123	1.6814	0.5	0.7123	1.7085

The effects of various salts and of hydrochloric acid on the potential of dilute solutions of molybdocyanide-molybdicyanide are shown in table 3. Instead of reporting the measured values of the E.M.F., the figures are given

for $\log \frac{f_3}{f_4}$ calculated from the equation:

$$E = \epsilon_0 + 0.059 \log \frac{C_{\text{MoCn}_6^{---}}}{C_{\text{MoCn}_6^{---}}} \cdot \frac{f_3}{f_4}$$

where E is the measured potential referred to the normal hydrogen electrode and ϵ_0 is the potential at infinite dilution (0.7260 volt). For the sake of brevity the composition of the very dilute molybdocyanide-molybdicyanide solution is omitted. Since these solutions were not

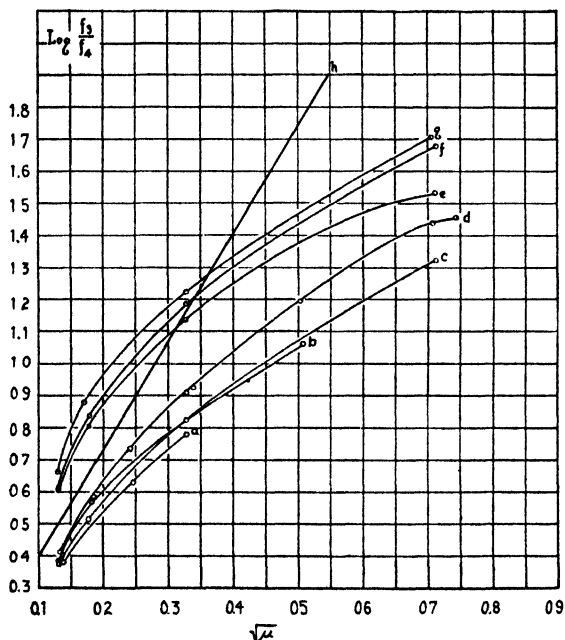


FIG. 4. Ratio of activity coefficients as a function of ionic strengths. a = HCl ; b = LiCl ; c = NaCl ; d = KCl and NH_4Cl ; e = CaCl_2 ; f = SrCl_2 ; g = BaCl_2 ; h = calculated values.

stable, fresh solutions had to be prepared for each set of measurements. $\sqrt{\mu}$ represents the square root of the total ionic strength of the mixtures, whereas μ_s designates the ionic strength of the added salts.

The values of $\log \frac{f_3}{f_4}$ are found plotted against $\sqrt{\mu}$ in figure 4. The straight line in figure 4 represents the theoretical values of $\log \frac{f_3}{f_4}$ calculated on the basis of the limiting Debye-Hückel equation.

The effect of various anions on the potential of a dilute solution of

molybdocyanide-molybdicyanide was investigated, using potassium chloride, potassium bromide, and potassium nitrate at a concentration of 0.25 molar, respectively, in the mixtures. The values of ϵ'_0 in the presence of the three salts were calculated from the measured E.M.F. as described above, and gave 0.7965, 0.7957, and 0.7950 volts, respectively. These results are in accordance with the results obtained in solutions of ferrocyanide-ferricyanide, the various univalent anions having virtually the same effect on the potential.

An attempt was made to determine the effect of sodium hydroxide on the potential of dilute solutions of molybdocyanide-molybdicyanide. Two solutions were measured, one containing 0.01 molar and the other 0.1 molar sodium hydroxide. The solutions were exceedingly unstable and no constant readings could be obtained. The potentials decreased very rapidly, but initial readings agreed with the values for ϵ_0 obtained with hydrochloric acid.

DISCUSSION OF THE RESULTS

The oxidation-reduction potential of the molybdocyanide-molybdicyanide system, starting at an ionic strength of zero, changes with increasing ionic strength markedly different from that of the ferrocyanide-ferricyanide system (3). In the latter case it was found that up to an ionic strength of 0.04, the normal potential was greater than that calculated on the basis of the limiting Debye-Hückel expression. With molybdocyanide-molybdicyanide, however, the experimental values were lower than the calculated ones at all ionic strengths. This behavior is normal in dealing with a system, the potential-determining ions of which are of such a high valence type. On the other hand, it should be stated that even at the greatest dilutions the slope of the experimental curve is decidedly less than that of the line calculated on the basis of the limiting Debye-Hückel expression. For this reason no attempt has been made to calculate average ionic sizes using the more extensive Debye-Hückel equation.

As was to be expected, neutral salts were found to increase the oxidation-reduction potential of dilute molybdocyanide-molybdicyanide solutions to a very large extent. With the univalent cations the effect decreases in the order $K^+ = NH_4^+ > Na^+ > Li^+ > H^+$. In all these cases the values of $\log \frac{f_3}{f_4}$ calculated from the experimental data were less than those derived from the simple Debye-Hückel expression. In the case of ferrocyanide-ferricyanide, however, the experimental figures at lower ionic strengths were less than the ones calculated from the Debye-Hückel equation.

The divalent cation salts, at the same ionic strengths, have a much greater effect, the latter decreasing with decreasing ionic size: $Ba^{++} >$

$\text{Sr}^{++} > \text{Ca}^{++}$. At lower ionic strengths the experimental figures for $\log \frac{f_3}{f_4}$ were found to be greater than those calculated on the basis of the simple Debye-Hückel expression. Hydrogen ions have an effect similar to that of other univalent cations, the former being comparable to the lithium ion. From this behavior one may infer that both molybdocyanic and molybdicyanic acids behave as strong electrolytes. In this respect molybdocyanic acid is entirely different from ferrocyanic acid, since it has been found that the fourth ionization constant of the latter is equal to 5.6×10^{-5} (4). This explains why the oxidation-reduction potential of the ferrocyanide-ferriocyanide system increases much more with increasing hydrogen-ion concentration than that of the molybdocyanide-molybdicyanide system.

SUMMARY

1. The normal potential of the molybdocyanide-molybdicyanide system was extrapolated to an ionic strength of zero and found to be 0.7260 volt at 25°C.
2. The effect of various salts upon the oxidation-reduction potential at various ionic strengths has been determined. The univalent anions investigated have the same effect at corresponding ionic strengths.
3. At the same ionic strengths divalent cations exert a greater effect than univalent cations, the effect decreasing with decreasing size of the ion.
4. From the effect of hydrogen ions upon the potential, it is concluded that molybdocyanic acid is a strong electrolyte.

REFERENCES

- (1) COLLEBERG, O.: Z. physik. Chem. **109**, 353 (1924).
- (2) FIESER, L. F.: J. Am. Chem. Soc. **52**, 5204 (1930).
- (3) KOLTHOFF, I. M., AND TOMSICEK, WM. J.: J. Phys. Chem. **39**, 945 (1935).
- (4) KOLTHOFF, I. M., AND TOMSICEK, WM. J.: J. Phys. Chem. **39**, 955 (1935).
- (5) OLSSON: Ber. **47**, 917 (1914).

THE ACTION OF POTASSIUM *n*-AMYL XANTHATE ON CHALCOCITE

A. M. GAUDIN AND REINHARDT SCHUHMANN, JR.

Ore Dressing Laboratories, Montana School of Mines, Butte, Montana

Received July 25, 1935

In the flotation concentration of ores, water-soluble substances such as xanthates, generally termed collecting agents, are used to prepare the surface of the minerals to be floated so that attachment will take place between air bubbles and the mineral particles. Very small quantities of xanthates (of the order of 0.05 lb. per ton of ore) are found entirely adequate to impart to the mineral particles a surface at which air will displace water to such an extent that efficient flotation is possible. At the present time the nature of the mechanism of this action is for the most part an unsettled matter.

In previous work with potassium *n*-amyl xanthate and chalcocite, Dewey (1, 3) found that cuprous xanthate and several other organic copper compounds could be leached from the surface of chalcocite which had been treated with potassium *n*-amyl xanthate under various conditions. He explained the formation of the organic copper compounds other than cuprous xanthate by "decomposition" and "association" hypotheses. In long-time grinding tests of potassium *n*-amyl xanthate and chalcocite nothing could be leached from the mineral. No effort was made to find the cause of this phenomenon and its relation to other results. Dewey also made experiments which indicated that oxygen is necessary for the reaction between xanthate and chalcocite, and unnecessary if dioxanthogen is substituted for the potassium xanthate. In Dewey's work as a whole, the experimental variables, time of grind, time of xanthate treatment, and amount of xanthate, had values far above those encountered in flotation practice. Also the desirability of working out and applying a quantitative technique to the determination of the reaction products of amyl xanthate and chalcocite was strongly indicated.

In the present investigation the primary aim has been to establish a sound experimental basis for the explanation of the mechanism of the collecting action of xanthates on chalcocite. For the xanthate treatment of chalcocite an experimental technique has been used which allows reasonably close laboratory reproduction of actual flotation operation procedure and conditions, and at the same time makes possible an accurate

accounting of all the reaction products. The influence of several experimental variables on the reaction product relationships was found, and the results were correlated with the flotative properties of the mineral. A group of tests was conducted to ascertain whether cuprous xanthate is adsorbed from benzene solution by chalcocite. For comparative purposes a few of the experiments were repeated using the oxidized mineral malachite instead of chalcocite.

EXPERIMENTAL

Materials

Chalcocite (Cu_2S) was obtained from a coarse, relatively pure Kennecott jig concentrate by consecutive hand picking, crushing, table concentration, sizing ($-28 +65$ mesh), then finally chemical cleaning with 1:1 hydrochloric acid, then concentrated aqua ammonia. This "cleaned chalcocite" was found to be quite pure, containing minute quantities of bornite (Cu_5FeS_4), chalcopyrite (CuFeS_2), and somewhat more covellite (CuS). A small batch of "cleaned chalcocite" was melted in a crucible, crushed, and sized ($-28 +65$ mesh) to give a product suitable for use. This artificial chalcocite has been termed "furnace chalcocite."

Potassium *n*-amyl xanthate was prepared from *n*-amyl alcohol (Sharples Solvents Corporation), carbon disulfide, and potassium hydroxide. The crude preparation was purified by recrystallization from an acetone-ether mixture, followed by a thorough washing with ether. Prepared in this way the xanthate is very slightly yellowish in color, practically odorless, and very voluminous. Iodometric titration of an aqueous solution showed the purity to be 99.5 per cent.

Cuprous *n*-amyl xanthate was prepared from potassium xanthate and cupric chloride in water or alcoholic solution according to the following reaction:



(In this and other equations in this paper, X is used to denote the amyl xanthate radical, $-\text{SC}(\text{S})\text{OC}_5\text{H}_{11}$.) It was found that the pure substance could be prepared by washing the yellow precipitate very carefully with alcohol and ether to remove the dixanthogen (X_2 , also known as amyl thioformate disulfide) also formed by the reaction. The cuprous *n*-amyl xanthate prepared in this way appeared non-crystalline, even under the microscope, but it was found that very small yellow prismatic crystals could be crystallized from pyridine.

General experimental procedure

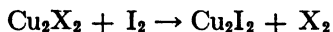
The procedure used may be summarized as follows: (1) A 200-g. charge of chalcocite was ground in a 500-g. capacity Abbé porcelain pebble mill

(4000 g. of pebbles) with 200 cc. of distilled water. (The empty space in mill was about 3 l., containing about 85 milliequivalents of oxygen at 615 mm. and 20°C.) (2) The pulp from (1), after dilution to 400–450 cc., was agitated with an accurately weighed amount of potassium *n*-amyl xanthate in a closed 2.5-l. reagent bottle. (3) The treated pulp was filtered and the mineral washed with water on a Buchner funnel, diluting the filtrate to 500 cc. for analysis. (4) The mineral was leached with acetone, ether, and warm benzene, in the order named. (5) The aqueous filtrate and the leach products were analyzed.

Analytical methods

The aqueous filtrate from the treatment of the chalcocite with xanthate was analyzed iodometrically for reducing ions and excess xanthate by the procedure of Taylor and Knoll (11). In some of the experiments titrations with 0.02 *N* hydrochloric acid were made to determine the total hydroxide plus carbonate. The total potassium in solution in several experiments was determined as potassium sulfate (12). Sulfate was determined by precipitation as barium sulfate (9).

As cuprous xanthate was found (as described later) to be the major leach product, an iodometric method was developed for its determination in benzene solution, utilizing the following reaction:



It was found that an accurate determination can be made on a 25-cc. aliquot portion of a benzene leach solution containing cuprous xanthate by titration with a 0.005 *N* solution of iodine in benzene, using a special technique. As the reaction is too slow to be practicable at ordinary temperatures, the titrations must be made near the boiling point of benzene, allowing 1–2 minute intervals with occasional shaking between 5-, 2-, or 1-cc. additions of iodine solution, the amount of iodine added depending upon the proximity to the end point as judged by experience. Titrating in this manner, the pink color of excess iodine becomes very noticeable with an excess of 0.5–1.0 cc. of 0.005 *N* iodine. This small excess may be quite accurately measured by color matching of the solution after removal of the cuprous iodide by filtration. Apparently the above reaction takes place in more than one step, as a dark brown solution is formed on first addition of the iodine, and no precipitate of cuprous iodide is formed until later stages in the titration.

REACTION PRODUCTS FOUND WITH THE CHALCOCITE

Leachable products

Dewey (1, 3), in his previous work on the reactions of potassium xanthate and chalcocite, was able to leach from the treated mineral a series of

six substances having different solubility properties. In the present work, with experimental conditions maintained as closely as possible within the limits of practical flotation operation, only two substances were leached from chalcocite treated with xanthate, as described in the following: (1) cuprous *n*-amyl xanthate, a yellow substance insoluble in ether, slightly soluble in acetone, and fairly soluble in benzene, forming a yellow solution; and (2) a red substance, soluble in acetone, ether, and benzene, forming orange to red solutions depending on the concentration. This substance was designated as "ether-soluble" to distinguish it from cuprous xanthate. Attempts were made to synthesize the "ether-soluble" compound in several ways from xanthate and monothiocarbonate, but no substance with the same solubility properties was obtained.

In all experiments it was found that the major portion of the leach products consisted of cuprous xanthate. From 100 to 1500 cc. of benzene were required for removal of the cuprous xanthate from the mineral, depending upon the amount present. As cuprous xanthate, even in an extremely weak solution, imparts a yellow color to benzene, the leaching was continued until the extract was colorless. The end point was quite definite, and little washing was required to finish the operation after the bulk of the cuprous xanthate had been removed.

The acetone leach, containing a little cuprous xanthate and perhaps a large part of the "ether-soluble," was evaporated (using a fan), and the "ether-soluble" and the cuprous xanthate in the residue separated by means of ether. The "ether-soluble" was combined with the main ether leach solution, evaporated, and the residue taken up with benzene for iodometric titration by the method used for the cuprous xanthate. The cuprous xanthate separated from the acetone extract was combined with the bulk of the cuprous xanthate for determination of the total cuprous xanthate.

Film at mineral surface unleachable by acetone, ether, and benzene

Using the leaching agents, acetone, ether, and benzene, a considerable portion of the xanthate abstracted by the chalcocite from an aqueous potassium amyl xanthate solution remained with the mineral in an unleachable state. This unleachable film decomposed, producing a pleasant ester-like odor, when the treated mineral was allowed to stand for a few days in a loosely stoppered bottle. On agitation with water of the treated chalcocite which had developed the characteristic odor, an appreciable frothing was noted, indicating the presence of a soluble surface-active organic compound.

It was found that by heating the xanthate-treated and leached chalcocite to about 220°C. in a distillation apparatus suitable for the distillation of very small quantities, a colorless, pleasant-smelling liquid could be

distilled off. Potassium amyl xanthate and other xanthate derivatives gave the same distillation product when heated in the presence of finely ground, untreated chalcocite, which presumably contained a little moisture not removed by the drying after grinding. The distillate was not a sulfur compound. The refractive index and boiling point checked those of amyl alcohol quite closely.

Attempts were made to remove the unleachable film with most of the common laboratory reactants and solvents, and a few rather uncommon ones. Except for pyridine, all the agents tried met with no success. The pyridine extract of xanthate-treated and leached (acetone, ether, and benzene) chalcocite was yellow. Evaporation of the yellow pyridine solution showed the substance removed to be cuprous xanthate. Thus, the unleachable film *appears* to be cuprous xanthate so intimately associated with the chalcocite that a chemically active agent is necessary to break it away.

THE EFFECT OF QUANTITY OF XANTHATE

The effect of quantity of xanthate on products of treatment

A series of experiments was made using the experimental procedure previously described to find the effect of quantity of xanthate added on the products of the action of potassium *n*-amyl xanthate on chalcocite. The grinding time and xanthate treatment time in this series were kept constant at one hour and at fifteen minutes, respectively. Results are given in table 1, and graphically represented in figures 1 and 2.

In this group of experiments the "ether-soluble" leach product was quite small in quantity in comparison with the cuprous xanthate, having from 1 to 4 per cent of the iodine equivalent of the cuprous xanthate leached. Enough of the red "ether-soluble" substance for an analysis was not obtained. Since the amount was so small, it was included with the cuprous xanthate in the table of results. As a matter of fact, in most of the tests only the total amount was determined by titration of the combined leach products, as the very small quantity of "ether-soluble" material was not observed and differentiated from cuprous xanthate until some of the tests with larger quantities of xanthate had been conducted.

Two experiments were made using "furnace chalcocite" in place of the "cleaned chalcocite." Under like conditions the proportion of products was roughly the same as for the unmelted mineral. The little difference was probably due to the difference in grinding properties between the natural and artificial copper sulfides. These two experiments showed that porosity or some other property peculiar to the chemically cleaned mineral was not an important determinative factor in the results.

In this series of tests it is seen that the xanthate added may be accounted for as excess xanthate in solution, leachable compounds (practically all

TABLE 1

The effect of quantity of xanthate added on the reaction products

200 g. of cleaned chalcocite, 1-hour grind in 500-g. pebble mill with 4000 g. of pebbles, conditioned 15 minutes on mechanical rolls in 2.5-l. bottle with 0.5 l. of water and potassium *n*-amyl xanthate as indicated. Amounts expressed as milliequivalents per 200 g. of chalcocite. The symbol X is used for the xanthate radical.

KX ADDED	Cu_2X_2 EX- TRACTED	EXCESS X IN SOLUTION	TOTAL X- ABSTRACTED	UNLEACH- ABLE X ON CHALCO- CITE*	TOTAL OH^- , CO_3^{--} IN SOLUTION	SO_4^{--} IN SOLUTION	TOTAL ANIONS IN SOLUTION	K^+ IN SOLUTION
0.25	0.007		0.25	0.24				
0.50	0.058		0.50	0.44				
1.10	0.46	0.01	1.09	0.63				
1.61	0.81	0.01	1.60	0.79				
2.67	1.80	0.02	2.65	0.85				
2.66	1.65	0.02	2.64	1.00	2.12	0.20	2.34	
4.21	2.86	0.02	4.19	1.33				
4.21	2.80	0.02	4.19	1.39				
6.31	4.64	0.09	6.22	1.58	5.50			6.31
8.55	6.00	0.95	7.60	1.60	6.35			8.34
10.64	6.52	2.42	8.22	1.70	7.13			10.50
12.90	7.02	4.19	8.71	1.69	8.00	0.30	12.57†	12.73

* Obtained by difference.

† Including reducing ions, $(\text{S}_m\text{O}_m)^{--}$. In most of the tests the reducing ions were negligible, increasing with xanthate added to a maximum of 0.08 milliequivalent for 12.90 milliequivalents of xanthate added.

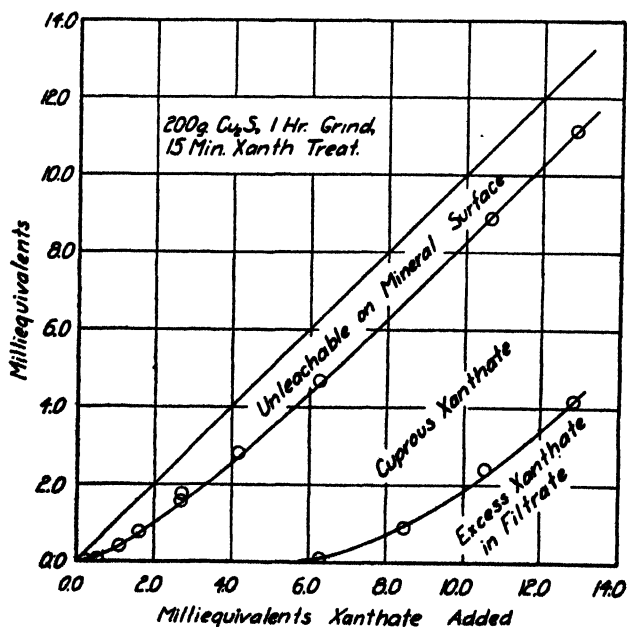


FIG. 1. The effect of quantity of xanthate added on the reaction products

cuprous xanthate), and unleachable xanthate, the proportions of these three being dependent on the quantity of xanthate added. The unleachable portion tends to approach a maximum with increasing amount of xanthate added.

All the potassium of the collector remains in solution, and hydroxide, carbonate, and sulfate are thrown into solution to make a total equivalent to the xanthate taken out of solution, within the limits of experimental error. Under the conditions of these tests, reducing ions (S_mO_n)—thrown into solution were practically negligible, in no experiment amounting to over 0.08 milliequivalent per 200 g. of chalcocite.

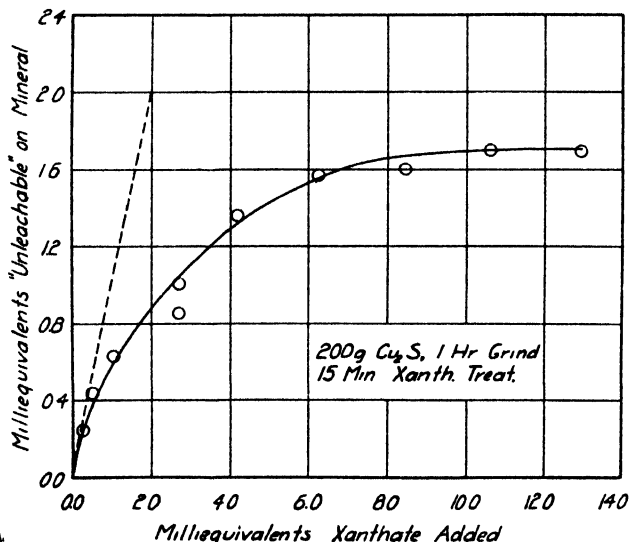


FIG. 2. The effect of quantity of xanthate added on the unleachable xanthate on the chalcocite

Flotation tests were made on leached and unleached treated chalcocite. These tests were made in a 50-g. celluloid cell with no further addition of reagent, either frother or collector. They showed that the removal of leachable products had no appreciable effect on the floatability of the xanthate-treated mineral; 95 to 100 per cent recovery could be obtained in all the tests but that involving the smallest amount of xanthate. In the tests involving larger amounts of xanthate the froth was very dry and the chalcocite seemed to float very peculiarly, more as a "dust" than as a mineralized froth. In the tests in which the maximum unleachable quantity was closely approached, the mineral floated immediately upon addition to the machine as an apparently dry mass which could be literally blown out of the machine. Gaudin and Malozemoff (4) observed this phenomenon of an extremely dry froth with both galena and chalcocite under certain conditions. This condition might correspond to an air-

solution-mineral contact angle in the neighborhood of 90°, the result perhaps of a complete filming on the mineral particles by the unleachable xanthate.

The effect of quantity of xanthate on flotation recovery

Flotation tests on 40-g. samples of ground chalcocite were made in a 50-g. capacity celluloid "University of Utah" cell with the addition of terpeneol, 0.05 lb. per ton, and varying amounts of potassium *n*-amyl xanthate. The chalcocite was ground in 200-g. batches according to the

TABLE 2

The effect of quantity of xanthate added on the flotation recovery

40-g. samples floated in 50-g. celluloid cell with terpeneol, 0.05 lb. per ton, for 6-8 minutes after 2 minutes conditioning with amount of potassium *n*-amyl xanthate as indicated.

LBS. OF XANTHATE PER TON OF CHALCOCITE	MILLIEQUIVALENTS OF XANTHATE PER 200 G. OF CHALCOCITE	RECOVERY PER CENT
15-minute grind		
0.00	0.00	13
0.025	0.013	31
0.14	0.07	65
0.28	0.14	83
0.41	0.20	85
1-hour grind		
0.00	0.00	7
0.005	0.0025	10
0.055	0.027	31
0.11	0.053	41
0.16	0.08	54
0.21	0.10	66
0.25	0.12	70
0.39	0.20	75
0.51	0.26	85

procedure previously described, flotation data being obtained for two grinding times, fifteen minutes and one hour, respectively. Mohr pipettes were used to add a standard xanthate solution directly to the pulp in the cell. Two minutes after the xanthate collector addition the frother was added and the froth raked off for 6 to 8 minutes. Concentrates and tailings were weighed and the recoveries calculated. Results are given in table 2 and graphically represented in figure 3.

From the data for the chalcocite ground for one hour it is seen that 0.26 milliequivalent of potassium *n*-amyl xanthate per 200 g. of chalcocite

is sufficient for substantial flotation. From table 1 it is seen that if this amount of xanthate is added to 200 g. of chalcocite ground for one hour, practically all of the xanthate abstracted by the mineral is unleachable. Also, under these conditions the amount of unleachable product on the mineral is only about one-seventh of the maximum possible unleachable amount for the quantity of mineral and time of grind in question, as indicated by the curve of figure 2. If this unleachable entity corresponds to a monomolecular film (as will be shown hereafter), it can thus be said that only a fraction of a monomolecular film is necessary for flotation of a particle. Comparison of the data for the two times of grind confirms this line of reasoning by showing that the quantity of xanthate required for a

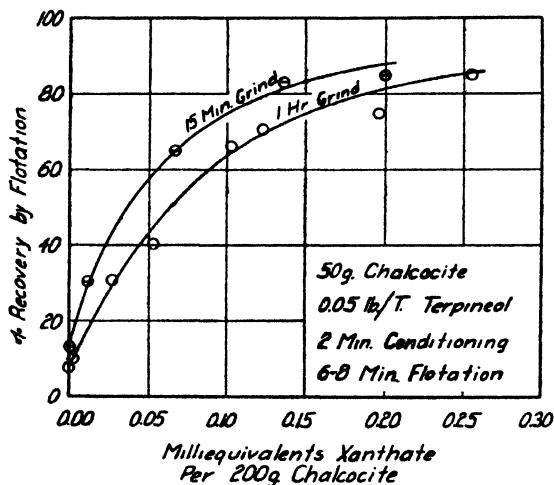


FIG. 3. The effect of quantity of xanthate on the flotation recovery

given flotation recovery is dependent upon the fineness of grinding, and therefore, on the area of mineral surface.

The froth dryness-contact angle analogy previously suggested gives weight to the idea of only a partial monomolecular film with a surface of relatively low contact angle being necessary for high flotation recovery. To use another terminology, the mineral particles do not have to be treated to the maximum degree of non-wettability but only to a certain fraction of that degree, the value of that fraction being dependent upon particle size, shape, and specific gravity. Mathematical calculations of the theoretical order of magnitude of the contact angle necessary for flotation made by Gaudin (2) led to the conclusion that particles are floatable with contact angles under 10° ; whereas Wark and Cox (13) experimentally found the maximum contact angle of minerals in contact with amyl xanthate solution to be of the order of 90° .

THE EFFECT OF TIME OF XANTHATE TREATMENT

Several experiments were made varying the time of treatment with potassium *n*-amyl xanthate. The time of grind was one hour in all of this group of experiments. Results are given in table 3.

In the experiments involving long-time agitation with xanthate, appreciable amounts of the "ether-soluble" substance in addition to the cuprous xanthate were obtained by leaching. This red substance was apparently the same as the "ether-soluble" leach product observed in previous work with fifteen minutes treatment; in long-time agitation tests this substance was present in somewhat greater quantities. It seems likely that the

TABLE 3

The effect of time of xanthate treatment on the reaction products

Tests using general experimental procedure, grinding for 1 hour. Amounts expressed in milliequivalents per 200 g. of chalcocite. The symbol X is used for the xanthate radical.

KX ADDED	TIME OF TREATMENT	Cu ₂ X ₂ EXTRACTED	EXCESS X- IN SOLUTION	TOTAL X- ABSTRACTED	I ₂ EQUIV- ALENT OF "ETHER- SOLUBLE"	UNLEACH- ABLE X ON CHALCOCITE*	TOTAL OH ⁻ , CO ₃ ⁻ IN SOLUTION
2 62	1 min.	1.58	0 02	2.60		1.02	2.16
2.66	6 min.	1 56	0 02	2.64		1.06	2.12
2.66	15 min.	1.65	0.02	2.64		1.00	2.12
2 68	24 hrs.	0 95	0.02	2.66	0.28	†	1.63
10.70	1 min.	5.13	4.00	6 70		1.57	5.88
10.64	15 min.	6.52	2.42	8.22		1.70	7.13
10.63	20 hrs.	7 75	0.15	10 48	0.30	†	9.23

* Obtained by difference.

† The formula of the "ether-soluble" product is unknown, hence there is no basis for a calculation of the unleachable quantity when an appreciable quantity of "ether-soluble" is found.

"ether-soluble" material is a reaction product, possibly containing the monothiocarbonate radical, formed slowly in long-time treatment from cuprous xanthate, free hydroxide, and chalcocite, as suggested by Dewey in his "decomposition" and "association" hypotheses. Oxygen may also enter the reaction.

Evidently the reactions to produce the unleachable film and the cuprous xanthate occur immediately on mixing the reagent with the pulp. However, from the results with the larger quantity of xanthate it seems that the cuprous xanthate formation slows up as more cuprous xanthate coating is produced on the mineral, probably owing to difficulty of diffusion of free xanthate ions through the coating to react with the mineral.

RELATION OF EFFECTIVE MINERAL SURFACE AREA TO PRODUCTS

Effect of time of grinding

A series of experiments was made to determine the effect of time of grinding on the reaction-product relationships. The usual experimental

TABLE 4

The effect of time of grinding on the reaction products

Tests using general experimental procedure, treating with 5.4 milliequivalents of potassium *n*-amyl xanthate for 15 minutes. Amounts expressed as milliequivalents per 200 g. of chalcocite. The symbol X is used for the xanthate radical.

HOURS OF GRIND	Cu_2X_2 EXTRACTED	I ₂ EQUIVALENT OF "ETHER-SOLUBLE"	EXCESS X^- IN SOLUTION	UNLEACHABLE X ON CHALCOCITE*	MILLIEQUIV HCl TO YIELD A pH OF 7	REDUCING IONS IN SOLUTION
¼	3 80	0 06	1 04	0 80	2 96	0 03
1	From curve of figure 2			1 48		
2	3 52	0 11	0 02	1 81	3 59	
4	2 67	0 18	0 02	2 63	3 44	0 11
12	1 09	0 19	0 04	4.13	2 97	0 22
48	0 03†		0 01	4 46	0 37	

* Obtained by difference.

† The small quantity of "ether-soluble" in this run did not justify its separate determination, and it was added to the cuprous xanthate solution before titration.

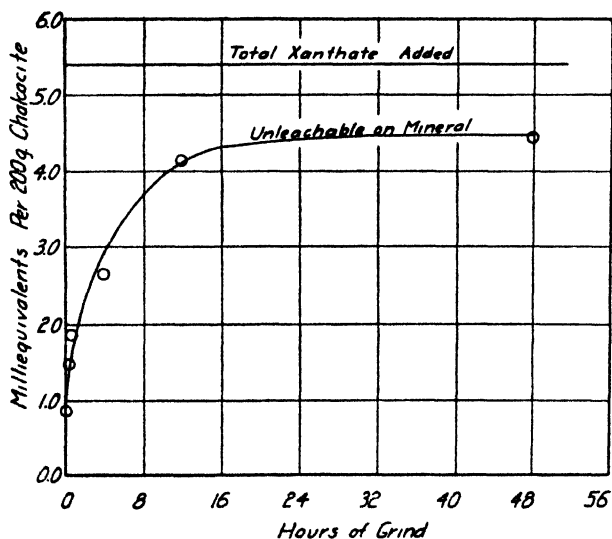


FIG. 4. The effect of time of grinding on the reaction products

procedure was used, the quantity of xanthate being kept constant at 5.4 milliequivalents and the xanthate treatment time being kept constant at

fifteen minutes. Experimental results are given in table 4 and plotted in figure 4.

In the longer grinding tests a considerable vacuum was noted on opening the pebble mill, indicating reaction of oxygen with the mineral during grinding. Increasing difficulty in filtration of the treated pulp was encountered with increasing fineness of grinding. Silicate in the ground pulp, worn off the pebbles, increased to about 10 to 15 per cent of the weight of the mineral for the longest grinding time.

The data from these runs show that the unleachable portion definitely increases with increase in surface of the mineral particles with longer grinding, and in long grinds approaches the total amount of xanthate

TABLE 5
Size analysis of destlimed ground chalcocite

SIZE	AVERAGE SIZE	THEORETICAL SPECIFIC SURFACE†	WEIGHT, PER CENT	THEORETICAL SURFACE‡
microns	microns	cm. ² per gram		cm. ² per gram
-74 (+200 mesh)	80	140	0.5	0.7
-74, +37 (-200, +400 mesh)	50	220	5.0	11
-37, +15	21*	520	25.4	184
-15, +7.5	10*	1100	57.9	637
-7.5	2†	5500	1.2	66
Total			100.0	899

* The accuracy of the average size figures from sedimentation analysis is probably of the order of 10 per cent. The figures are calculated assuming Stokes' law for spheres falling in a liquid; the irregularity in shape of ground mineral particles limits the accuracy of the method.

† This is an estimate, as no further separation was made of the -7.5 μ portion. The figure is purposely low, to be on the safe side. The weight per cent of this portion is so small that the soundness of the estimate has no great effect on the accuracy of the total surface figure.

‡ Assuming all particles to be cubes.

added. The titration figures on the filtrate show that the hydroxide decreases, while the reducing ions (S_mO_n)-- increase with increase in surface. Although no determinations were made, it is expected that the sulfate in the filtrate also increases with increase in time of grinding.

Estimation of thickness of unleachable film

As the phenomena associated with the formation and presence of the unleachable entity on the mineral surface seemed to be indicative of an irreversible adsorption, it seemed desirable to make a quantitative comparison of the extent of mineral surface and the maximum amount of unleachable attainable with that surface. The mineral which had been

ground in the pebble mill contained too large a percentage of extremely fine material for accurate surface measurement; accordingly for this work the mineral, after grinding, was carefully "deslimed" by water sedimentation in buckets. A sample of the deslimed mineral was then sized by combined screening and acetone sedimentation, and from the sizing analysis the surface was estimated. Results of this operation are given in table 5. In other work with the determination of surface area by sizing (5) it has been shown that a correction factor should be applied to the theoretical surface figure to correct for irregularity in shape of particles, cracks, etc. A factor of 1.5 was used, giving an actual surface figure of 1350 cm.² per gram (1.5×899). The factor used is possibly accurate to within 10 per cent; and as the theoretical surface figure is estimated to be accurate to about 10 per cent, the accuracy of the actual surface figure may be roughly 15 per cent ($\sqrt{0.10^2 + 0.10^2} = 0.141$).

Two samples of the sized chalcocite were agitated with a large excess of xanthate (2.5 and 1.5 milliequivalents per 150 g., respectively) and the products determined, using the general experimental procedure. The unleachable xanthate figures were 0.16 and 0.13 milliequivalents per 150 g., respectively. Using the average figure, 0.145 milliequivalent,

$$0.145 \times 10^{-3} \times 6.06 \times 10^{23} = 8.8 \times 10^{19} \text{ molecules of xanthate per 150 g. of chalcocite}$$

$$1350 \times 150 = 2.02 \times 10^6 \text{ cm.}^2 \text{ of surface per 150 g. of chalcocite}$$

Assuming a monomolecular film,

$$\frac{2.02 \times 10^6}{8.8 \times 10^{19}} = 23 \times 10^{-16} \text{ cm.}^2 = 23 \text{ A. U.}^2, \text{ the area occupied by one xanthate group}$$

Adam and Müller (10), by two independent methods, estimated the area of a hydrocarbon chain to be 20.5 A.U.², which agrees well with the figure of 23 A.U.² found here for the area occupied by one xanthate radical. The difference between these figures is well within the limits of experimental error of the method used in this work for the estimation of the surface of the chalcocite. Also the polar group of the xanthate radical may have some effect on the area which it occupies. Thus the result of the calculation justifies the assumption of a monomolecular film, and it can be said that the maximum amount of unleachable xanthate attainable on a chalcocite surface is equivalent to a complete monomolecular film.

ADSORPTION OF CUPROUS XANTHATE FROM BENZENE

Tests were run to determine if cuprous xanthate is adsorbed from benzene solution by chalcocite. 200-g. samples of chalcocite were ground

in a pebble mill for one hour with 500 cc. of benzene solutions of cuprous xanthate of various concentrations. Results of four such tests are given in table 6.

The chalcocite after these tests was found to be quite floatable in water. No cuprous xanthate could be removed from it by leaching with benzene. Pyridine, however, removed cuprous xanthate. Thus an "unleachable" film similar to that of the potassium xanthate treatment experiments, to which high mineral floatability is due, is also formed by the adsorption of cuprous xanthate from benzene. Also, the maximum unleachable figures for the two types of experiments seem to check, although this benzene adsorption series is too incomplete for a definite assertion. More detailed work of this nature might lead to interesting and significant results.

TABLE 6

Adsorption of cuprous xanthate from benzene by chalcocite

MILLIEQUIVALENTS OF Cu_2X_2 ADDED	MILLIEQUIVALENTS OF Cu_2X_2 LEFT IN SOLUTION	MILLIEQUIVALENTS OF Cu_2X_2 ADSORBED
0.40	0.00	0.40
0.89	0.23	0.66
1.34	0.54	0.80
3.43	1.73	1.70

COMPARATIVE TESTS WITH MALACHITE

A few semiquantitative experiments of the same nature as some of the chalcocite experiments were repeated with malachite, $(\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2)$. Two tests were made on 200-g. samples, using the general experimental procedure for grinding, treatment, and determination of reaction products. It was found that malachite abstracts xanthate from aqueous potassium *n*-amyl xanthate solution, forming cuprous xanthate and dixanthogen. The malachite after the leaching procedure, contrary to experience with chalcocite, was entirely non-floatable. Thus, with malachite, an *unleachable* water-repellent coating is not formed in an aqueous xanthate solution.

Several tests with a benzene solution of cuprous xanthate showed that malachite does not appreciably adsorb the cuprous xanthate from benzene solution under the conditions under which chalcocite exhibits a marked adsorption.

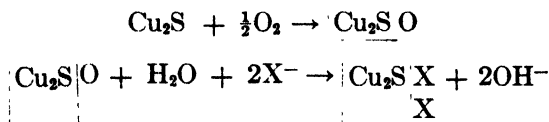
DISCUSSION

On the basis of the results presented in this paper it seems that the collecting action of xanthate is essentially different for chalcocite and for malachite. Apparently, the flotation of the sulfide mineral is caused by the formation of an oriented monomolecular film tightly "anchored" to the mineral; whereas flotation of the oxidized mineral seems to be due to

the formation of a much thicker coating of base-metal xanthate (and dixanthogen), not "anchored" to the mineral, but merely adjacent to the mineral surface. This comparison offers a rational explanation for the fact that in actual flotation operation the quantity of xanthate required for flotation of malachite is many times that required for flotation of chalcocite.

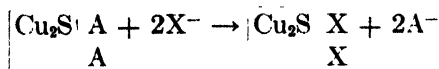
The "anchored" monomolecular film formed on chalcocite does not possess the same solubility properties as any known xanthate or xanthate derivatives. Although, as evidenced by its complete insolubility in benzene, the film does not consist of cuprous xanthate, cuprous xanthate may be removed from the surface by means of pyridine. On the whole, all the observed properties of this film seem to be analogous in many ways to the properties of films of adsorbed gases on solids, which were observed and clarified by Langmuir (6). Quoting from his discussion of the adsorption of oxygen on tungsten: "It is very evident from this work that the oxygen layer has totally different properties from those we should expect, either with a layer of oxide or a film of highly compressed gas. The facts are in good accord, however, with the theory that oxygen atoms are chemically combined with the tungsten atoms." On the basis of these and other similar results Langmuir advanced the theory that in the adsorption of gases on solids, the adsorptive forces are chemical forces of the primary valence type. Carrying this conception over to the present work, it appears that the "unleachable" film consists of xanthate groups chemically attached to copper atoms of the chalcocite by primary valence bonds.

The adsorbed film is formed on the chalcocite from potassium xanthate solution by reaction of the xanthate ions with the surface of the mineral. As suggested by Frumkin (8) for adsorption of electrolytes by charcoal, hydroxide ions are produced at the surface from adsorbed oxygen; these hydroxide ions are replaced by xanthate ions and enter the solution, as follows:

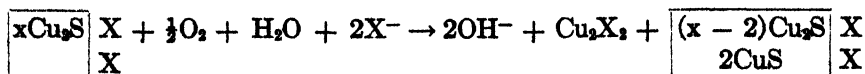


Carbonate ions may be formed from hydroxide and the carbon dioxide present in the system.

During grinding and other treatment, a certain amount of adsorbed or "anchored" reducing ions and sulfate ions are produced at the mineral surface by oxidation reactions, as suggested by Taylor and Knoll (11) for galena. These ions are also replaced by xanthate and enter the solution, as follows: (A denotes adsorbed anion, sulfate ion, reducing ion, etc.)



Cuprous xanthate is formed by reaction of xanthate ions with that part of the chalcocite surface already covered with an adsorbed xanthate film, as follows:



The cuprous amyl xanthate so formed is leachable with benzene, and its removal does not appreciably affect the flotative properties of the mineral. With the amounts of xanthate used in flotation practice only a relatively small fraction of the amount of reagent may be accounted for as cuprous xanthate.

THEORETICAL FORMULATION

Applying the kinetic theory of reaction to the suggested reaction mechanism, a mathematical interpretation of the reaction-product relationships given in table 1 may be obtained. The following symbols are used in the derivation:

A = milliequivalents of xanthate ions in solution at any time,

A_0 = total milliequivalents of xanthate extracted by the mineral from solution in a given reaction,

B = milliequivalents of adsorbed xanthate on mineral at any time,

B_0 = total adsorbed xanthate formed in a given reaction,

C = milliequivalents of cuprous xanthate on mineral at any time,

t = time,

S = effective mineral surface, expressed as milliequivalents of "elementary spaces" (see Langmuir (7)),

x = fraction of elementary spaces on which xanthate is adsorbed at any time,

x_0 = fraction of elementary spaces on which xanthate is adsorbed after completion of the given reaction, and

k_1, k_2, k_3 = constants.

First, the rate of decrease in free xanthate ions is equal to the sum of the rates of formation of adsorbed xanthate and of cuprous xanthate, as the loss in free xanthate in solution must be accounted for either as cuprous xanthate or as adsorbed xanthate.

$$-\frac{dA}{dt} = \frac{dB}{dt} + \frac{dC}{dt} \quad (1)$$

The rate of formation of adsorbed xanthate is proportional to the area of bare, unreacted surface and to the concentration of xanthate.

$$\frac{dB}{dt} = k_1(1-x)SA \quad (2)$$

The rate of formation of cuprous xanthate is proportional to the covered surface and to the concentration of xanthate.

$$\frac{dC}{dt} = k_2 x SA \quad (3)$$

Substituting equations 2 and 3 in equation 1,

$$-\frac{dA}{dt} = k_1(1 - x)SA + k_2 x SA \quad (4)$$

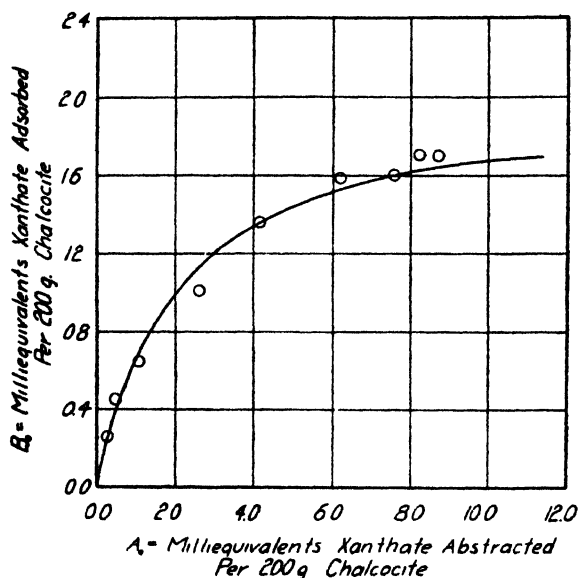


FIG. 5. Adsorption curve, $A_0 = -1.25B_0 - 9.1 \log (1 - B_0/1.75)$. Experimental points from table 1 plotted as circles

The rate of increase in adsorbed xanthate is equal to the rate of increase in adsorbed surface, expressed in the same units.

$$\frac{dB}{dt} = \frac{Sdx}{dt} \quad (5)$$

From equations 2 and 5,

$$\frac{dx}{dt} = k_1(1 - x)A \quad (6)$$

Dividing equation 4 by equation 6,

$$\frac{dA}{dx} = -S - \frac{k_2 x S}{k_1(1 - x)} = -S \left(1 + k_3 \frac{x}{1 - x} \right) \quad (7)$$

Integrating and substituting limits,

$$\frac{A_0}{S} = x_0(1 - k_3) - k_2 \log_e(1 - x_0) \quad (8)$$

Substituting data from table 1, $B_0 = x_0 S = 1.36$ when $A_0 = 4.19$, and assuming S , the surface for 1-hour grind, to be 1.75 milliequivalents as indicated by the maximum of the curve of figure 2, solving for the constant k_3 , and converting logs to base 10, the equation becomes:

$$A_0 = -2.19x_0 - 9.1 \log(1 - x_0) \quad (9)$$

Substituting $x_0 = B_0/S$

$$A_0 = 1.25B_0 - 9.1 \log(1 - B_0/1.75) \quad (10)$$

The curve of this equation is plotted in figure 5, with the experimental points from table 1 shown as circles. It is seen that the experimental points check this theoretical curve quite closely, especially as the experimental results for the adsorbed or "unleachable" entity were determined by difference from three experimental values: namely, the total xanthate added, the cuprous xanthate extracted, and the excess xanthate in solution.

SUMMARY AND CONCLUSIONS

In this work the following results have been obtained:

1. In short-time treatment of chalcocite with xanthate the xanthate abstracted by the mineral may be accounted for as cuprous xanthate and as an entity unleachable with ordinary solvents. The formation of these two products occurs practically instantaneously, although with larger quantities of xanthate the reaction to form cuprous xanthate slows up with increase in quantity of cuprous xanthate on the mineral.

2. In long-time treatment of chalcocite with xanthate, leachable products other than cuprous xanthate are formed relatively slowly, possibly by reaction of cuprous xanthate and hydroxide in solution.

3. All the potassium of the potassium xanthate remains in the solution.

4. Hydroxide, carbonate, sulfate, and reducing ions $(S_mO_n)^{-}$ are thrown into the solution in a total amount metathetically equivalent to the xanthate abstracted from the solution.

5. Leaching off the leachable products from xanthate-treated chalcocite has no appreciable effect on the flotative properties of the chalcocite.

6. Pyridine extracts cuprous xanthate from xanthate-treated and leached chalcocite, that is, from chalcocite having the "unleachable" film.

7. The "unleachable" product increases with increase in xanthate added, approaching a maximum in a manner suggestive of adsorption.

8. The maximum amount of unleachable xanthate attainable with a given sample of chalcocite corresponds to a complete monomolecular film on the chalcocite.

9. If a quantity of xanthate just sufficient for effective flotation is added, it may be almost completely accounted for as the unleachable product. Only a relatively small fraction of a monomolecular film of "unleachable" is necessary for efficient flotation. The fraction of the surface filmed determines the dryness of the mineralized froth.

10. Increasing the surface of the mineral by longer grinding increases the unleachable portion and decreases the cuprous xanthate portion of the reaction products.

11. The unleachable water-repellent film may be produced by the adsorption of cuprous xanthate from benzene solution by the chalcocite.

12. There is an essential difference between the collecting actions of xanthate on chalcocite and on malachite, respectively. An unleachable, water-repellent film is not formed on malachite by xanthate.

From these experimental facts it appears that the collecting action of xanthates in the flotation of chalcocite is a result of the production of an oriented, partial-monomolecular film of xanthate groups, chemically adsorbed in the Langmuirian sense. This film is formed by reaction of xanthate ions with the surface of the mineral which contains various adsorbed entities as a result of oxidation during grinding and other treatment. The formation of the adsorbed film is accompanied by reaction of a portion of the xanthate to form cuprous xanthate and perhaps small amounts of other substances separable from the mineral by means of organic solvents. Application of kinetic theory principles to the suggested reaction mechanism gives an adsorption-reaction curve which checks the experimental data well within the limits of experimental error.

This work is being continued with other xanthates and other minerals.

REFERENCES

- (1) DEWEY, F. D.: Reactions of Some Sulfur-bearing Collecting Agents with Certain Copper Minerals. Thesis, Montana School of Mines, 1933.
- (2) GAUDIN, A. M.: Trans. Am. Inst. Mining Met. Engrs. **112**, 233 (1934).
- (3) GAUDIN, A. M., DEWEY, F. D., AND OTHERS: Trans. Am. Inst. Mining Met. Engrs. **112**, 319-47 (1934).
- (4) GAUDIN, A. M., AND MALOZEMOFF, P.: J. Phys. Chem. **37**, 597-607 (1933).
- (5) GROSS, JOHN: Trans. Am. Inst. Mining Met. Engrs. **112**, 120 (1934).
- (6) LANGMUIR, I.: J. Am. Chem. Soc. **38**, 2267-78 (1916).
- (7) LANGMUIR, I.: J. Am. Chem. Soc. **40**, 1361 (1916).
- (8) See PEARCE, J. N.: J. Phys. Chem. **36**, 1980 (1932).
- (9) PREGL: Quantitative Organic Microanalysis. P. Blakiston and Sons, Philadelphia (1930).
- (10) See TAYLOR, H. S.: A Treatise on Physical Chemistry, 2nd edition, Vol. II, p. 1647. D. Van Nostrand Co., New York (1930).
- (11) TAYLOR, T. C., AND KNOLL, A. F.: Trans. Am. Inst. Mining Met. Engrs. **112**, 382-97 (1934).
- (12) TREADWELL, F. P., AND HALL, W. T.: Analytical Chemistry, Vol. II, p. 57. John Wiley and Sons, New York (1930).
- (13) WARK, I. W., AND COX, A. B.: Trans. Am. Inst. Mining Met. Engrs. **112**, 189 (1934).

A STUDY OF THE SORPTION OF ACID SODIUM OLEATE¹

R. F. NICKERSON²

Department of Chemistry, Massachusetts State College, Amherst, Massachusetts

Received August 1, 1935

The colloid theory of liquid-liquid systems has been envisaged in a broad, general formulation by Cofman (2), who redefined the classical thermodynamic variables and then applied them in the classical manner to colloid systems. One of the consequences of this approach is the statement that colloids are characterized by energy changes of a potential rather than a thermal nature. In other words, the energy exchanges of molecularly dispersed systems involve a heat effect which originates in the haphazard kinetic motion. On the contrary, the energy transfers of colloidally dispersed matter which, by definition, possesses a restricted degree of motion, must be associated with chemical or electrochemical processes. The same opinion had been expressed earlier by Einstein (2).

It is true that classical thermodynamics in the form of Gibbs' adsorption equation has proved to be both "infertile and incomplete" (16) for the liquid-liquid interface. Several reasons have been given for this failure, among which are the following: entropy changes in the adsorbing region contingent upon adsorption (10), inadequacy of the analytical methods employed to check the theory (10, 4), and the use of the equation in a questionably valid form (11).

The investigation reported here is a further study of the liquid-liquid interface by a method already outlined (15). The influence of some hydrocarbon oils on interfacial free energy is the subject of inquiry. The data are considered in the light of Cofman's theory.

METHOD

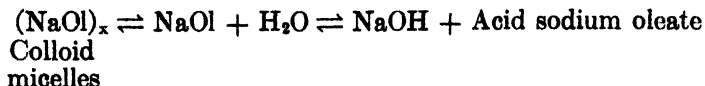
The method employed consisted of a study of the kinetics of sorption³ at the interface between sodium oleate solutions and hydrocarbon oils.

¹ Condensed from the dissertation presented to the Faculty of the Massachusetts State College in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1934.

² Present address: Worcester State Hospital, Worcester, Massachusetts.

³ McBain (11) applied the term "sorption" to surface effects that are not distinguishably adsorption or absorption.

Briefly the technique depends on the hydrolytic equilibrium



which has been worked out by McBain and his students (12, 14). It is evident that acid sodium oleate has the greatest escaping tendency of all the components of the equilibrium and, therefore, should be sorbed most readily. In the event of such sorption the equilibrium is displaced in the direction of formation of additional free sodium hydroxide.

The measurements of increments of sodium hydroxide were made at $25 \pm 0.01^\circ\text{C}$. with a conductivity apparatus. A 10-cc. volume of aqueous sodium oleate solution was introduced into a Freas type conductivity cell with attendant care to avoid frothing. Half an hour later the resistance of this solution was determined with a Wheatstone-Kohlrausch bridge sensitized with a two-stage audio frequency amplifier. Then, a 5-cc. aliquot of the hydrocarbon oil under investigation was allowed to run down the inside wall of the cell and to become an unbroken layer on the surface of the sodium oleate solution. The ground glass stopper of the conductivity cell was sealed with molten paraffin. Determinations of the resistance of the sodium oleate solution were recorded at specified intervals with time reckoned from the formation of the liquid-liquid interface.

MATERIALS

Sodium oleate was prepared from oleic acid of the best quality. Approximately molar equivalents of oleic acid and freshly made sodium alcoholate, both in absolute alcohol, were poured together. The precipitated sodium oleate was washed on a suction filter with cold absolute alcohol. The partially purified product was precipitated again from absolute alcohol, washed, and finally dried at reduced pressure and low temperature to avoid decomposition.

Solutions of sodium oleate were prepared by a special procedure in order to avoid foams, exposure in transference, and contamination from soft glass. The calculated quantity of dry sodium oleate was weighed and introduced into a dry glass-stoppered Pyrex bottle and the necessary amount of conductivity water added. Like the sodium oleate solutions of Du Noüy (3), solutions treated as described remained clear almost indefinitely, provided they were sealed with paraffin and stored in the dark.

Sodium hydroxide solutions were obtained from the dilution of 20 *M* sodium hydroxide with the proper amount of conductivity water (1).

The hydrocarbon oils—*o*-, *m*-, and *p*-xylenes, toluene, benzene, *n*-hexane, *n*-heptane, *n*-octane, 95 per cent *n*-nonane, *n*-decane, and kerosene—were purified by double distillation from metallic sodium through an

all-glass Pyrex distilling apparatus. The fraction of kerosene which distilled between 180 and 240°C. was taken as representative. The 95 per cent *n*-nonane was made available through the courtesy of the Bureau of Standards, American Petroleum Institute Project No. 4.

EXPERIMENTAL

New data have demonstrated that benzene, used in the previous study (15), is not a good standard of reference for the hydrocarbons. For this reason the sorption phenomenon was examined over a range of concentra-

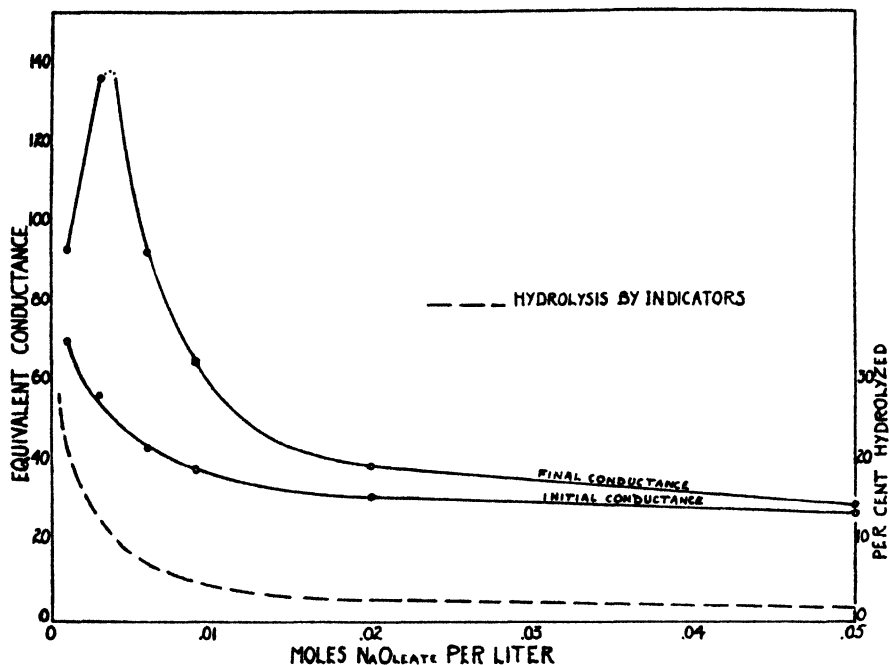


FIG. 1. Variations of the conductance induced by *m*-xylene with concentration of sodium oleate. Dotted line shows hydrolysis found by indicators

tions of sodium oleate with *m*-xylene superimposed. The layer of hydrocarbon oil on the surface of the dilute sodium oleate solution displaces the hydrolytic equilibrium in the direction of greater hydrolysis. The magnitude of the displacements can be estimated accurately as *increments* of the equivalent conductance of the aqueous phase.

The initial and final conductances of sodium oleate solutions over a range of concentrations are given in graphical form (figure 1), together with the percentages of normal hydrolysis obtained through indicators by McBain and Hay (13) in the same concentration interval. The final conductance was read after twenty-two hours.

Although the curve of percentages of sodium oleate hydrolyzed shows a rapid and continuous increase with dilution, the curve of final conductances under *m*-xylene is not symbatic. If the conductance increments were a measure simply of the phase distribution of oleic acid, the equivalent conductance of sodium hydroxide (240 mhos) should be approached. This is, however, not the case. After passing through a maximum, the final conductance begins to decrease in spite of the fact that normal hydrolysis increases.

These data indicate that the effect measured is not simply the extraction of free oleic acid by the oil phase but, rather, is a true adsorption at the interface.

TABLE 1
The sorption potentials of some hydrocarbons at 25°C.

OIL	INITIAL CONDUCTANCE	FINAL CONDUCTANCE	INCREMENT	SORPTION POTENTIAL
Hexane.....	36.72	49.33	{ 12.61 12.65	0.509
Heptane.....	38.30	50.77	12.47	0.503
Octane.....	38.20	50.56	12.36	0.498
Nonane.....	38.20	49.97	11.77	0.476
Decane.....	38.20	48.69	10.49	0.424
Benzene.....	36.51	55.15	{ 18.64 19.81	0.753? 0.801?
Toluene.....	36.10	58.00	21.90	0.885
<i>o</i> -Xylene.....	36.55	60.96	24.41	0.987
<i>m</i> -Xylene.....	36.35	61.12	{ 24.77 24.77	1.000
<i>p</i> -Xylene....	36.59	60.16	23.57	0.952
Kerosene.....	36.84	48.36	11.52	0.466

Sorption potentials of hydrocarbon oils

The conductance increments of a series of hydrocarbon oils have been determined. The hydrocarbons were investigated two at a time in closely similar cells. Simultaneously, with each pair a control determination was made on *m*-xylene. Aliquot parts (10 cc.) of the same *M*/100 sodium oleate solution were used for all of the hydrocarbons given in table 1. The ratio of the total conductance increment for a given hydrocarbon to that for *m*-xylene is tabulated as the relative sorption potential.

Rates of sorption of the hydrocarbons

The rate of sorption during the first few minutes of the process is an important datum for any hydrocarbon oil. This initial velocity is an

approximate measure of the potential gradient for acid sodium oleate between the aqueous solution and the liquid-liquid interface. In each portion of the same sodium oleate solution the thermodynamic potential of acid sodium oleate is the same; hence, the relative potential gradient is determined solely by the free interfacial energy. Therefore, the rate of sorption at the outset of the process is proportional to the free interfacial energy. The free sodium hydroxide which accumulates as a result of the displacement of the hydrolytic equilibrium complicates the subsequent rates and alters the thermodynamic potential of the acid soap.

The initial rate of sorption for each hydrocarbon oil has been calculated. The conductance increment for the first quarter of an hour of the velocity process was multiplied by four in order to convert it to mhos per hour.

TABLE 2

Relative initial free interfacial energies and total conductance increments in contact with $M/100$ aqueous sodium oleate solution

OIL	RELATIVE INTER- FACIAL ENERGY AS MHOS PER HOUR	TOTAL CONDUCT- ANCE INCREMENT
Hexane	3.68	12.6
Kerosene	2.56	11.5
Benzene	1.32	18.6
<i>p</i> -Xylene	1.40	23.6
Toluene	1.60	21.9
<i>m</i> -Xylene	6.72	24.8
<i>o</i> -Xylene	11.52	24.4

The first part of the conductance-time curve may be assumed to be linear without much error. These initial slopes or relative interfacial free energy values are given in table 2 for a few hydrocarbons.

The complete conductance-time data are given in figure 2 for all of the hydrocarbons except the alkanes heptane, octane, nonane, and decane. These alkanes differ only slightly from hexane; therefore they are omitted.

The curves demonstrate clearly that a disturbing factor exists in the case of benzene. The data in both tables 1 and 2 indicate a peculiarity also. Closer inspection of figure 2 has led to the suspicion that the same disturbance influences the toluene and *p*-xylene curves, although to a lesser degree.

The interpretation of these results is greatly simplified when the structure of surfaces given by Harkins, Clark, and Roberts (5) and Harkins, Davies, and Clark (6) is employed. These authors and Langmuir (9) have shown that the benzene ring, uniformly polarized by its double bonds, lies flat in the surface of pure water. Harkins and his collaborators have stated also that toluene molecules are slightly tilted as a result of the polarizing influence of the methyl group; *m*- and *o*-xylene make larger and larger

angles respectively with the plane of the interface. The intensity of the stray fields of these molecules varies with the angle of tilt.

The order of intensity of these stray electric fields adjudged from structure only should be *o*-xylene > *m*-xylene > toluene > *p*-xylene > benzene. The evidence given above (table 2) is in complete agreement with these conclusions of Harkins and Langmuir, and seems to indicate that the initial slope of the time sorption curve is a measure of the free interfacial energy present subject to the conditions imposed.

The work of McBain (14) and Walker (17) has elucidated the nature of the aqueous sodium oleate solutions. At the concentration ($M/100$) used in the present experiments sodium oleate is largely in the form of micelles.

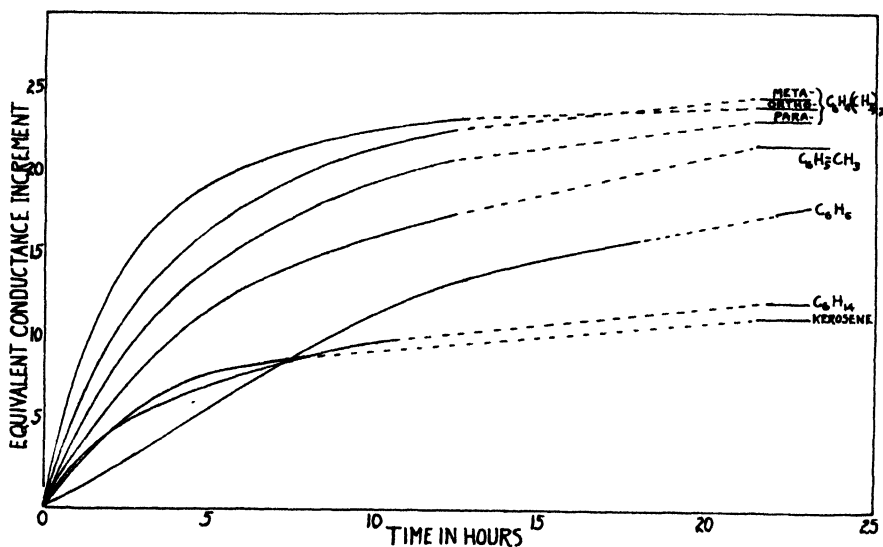


FIG. 2. The time increments of equivalent conductance for a few pure hydrocarbons. The solid lines indicate the readings taken.

These micelles are rather highly polar as a consequence of their structure. Surface tension measurements (7) show that colloid micelles of sodium oleate exert a much smaller surface pressure than molecular soap does. As concentration increases, the surface pressure of sodium oleate decreases after a maximum has been passed. It may be concluded, therefore, that the surface of a $M/100$ sodium oleate solution is somewhat polar in nature because the surface solute is principally in the form of polar micelles. Under these conditions the stray fields of the impinging hydrocarbons probably exist in almost the same relationship to the sodium oleate interface as they do to pure water.

The conductance measurements reported here are evidently due to the

selective sorption of acid sodium oleate. The selective sorption and orientation of molecular soap must of necessity destroy the polar nature of the aqueous surface, and create in its place a non-polar surface of oleate chains on which the hydrocarbon oil impinges. The end result, then, must be a re-orientation of the benzene rings and a straightening of the tilted rings to the perpendicular. The previously mentioned flattening of the time-conductance curves seems to be evidence of this phenomenon. The fact that benzene and all of its derivatives tend to nearly the same total increment regardless of initial slope, bears out this statement also. In accordance with Gibbs' minimum free energy principle any changes in surface structure must be in the direction of increases of potential energy. These re-orientation effects seem, therefore, to indicate "changes of entropy" in the adsorbing layers of the hydrocarbon oil.

Storage of potential energy

It has been suggested (2) that energy transfers in colloid systems involve chemical or electrochemical processes. Some support for this statement is contained intrinsically in the data above, but an experiment was designed to yield more direct proof. To the same $M/100$ sodium oleate solution known amounts of sodium hydroxide were added stepwise and aliquots of the sodium oleate-sodium hydroxide mixture were removed between additions. An accurately measured amount of each aliquot was investigated with *m*-xylene at 25°C. The data are plotted in figure 3.

The additional alkali suppresses normal hydrolysis. Some of the added sodium hydroxide disappears by combination with the acid sodium oleate. The straight line in figure 3 is the conductance-concentration curve expected if none of the sodium hydroxide combined. The shaded area shows the amount and limit of normal hydrolysis.

m-Xylene induces hydrolysis even in the presence of added alkali which has reduced normal hydrolysis to a negligible degree. It is probable, then, that Cofman's idea is wholly tenable. Free energy in the system is converted to potential energy. In this induced hydrolysis water is broken up into its constituent ions; free energy is thereby stored as electrochemical potential.

Acid sodium oleate and surface tension

The increments of equivalent conductance at different concentrations of sodium oleate are plotted in figure 4 for comparison with the surface pressure measurements of Johlin (8). Surface pressure is the force exerted by the surface solute against the surface tension of the pure solvent; numerically, it is the difference between the surface tension of the pure solvent and that of the solution.

The similarity of the two curves suggests that a part of the surface pres-

sure exerted by sodium oleate is a function of hydrolysis as measured by conductance. In concentrations of $0.02\ M$ and greater, sodium oleate exists largely in the form of micelles. It appears, therefore, that the micelles alone exert a surface pressure of about 46 dynes and that greater

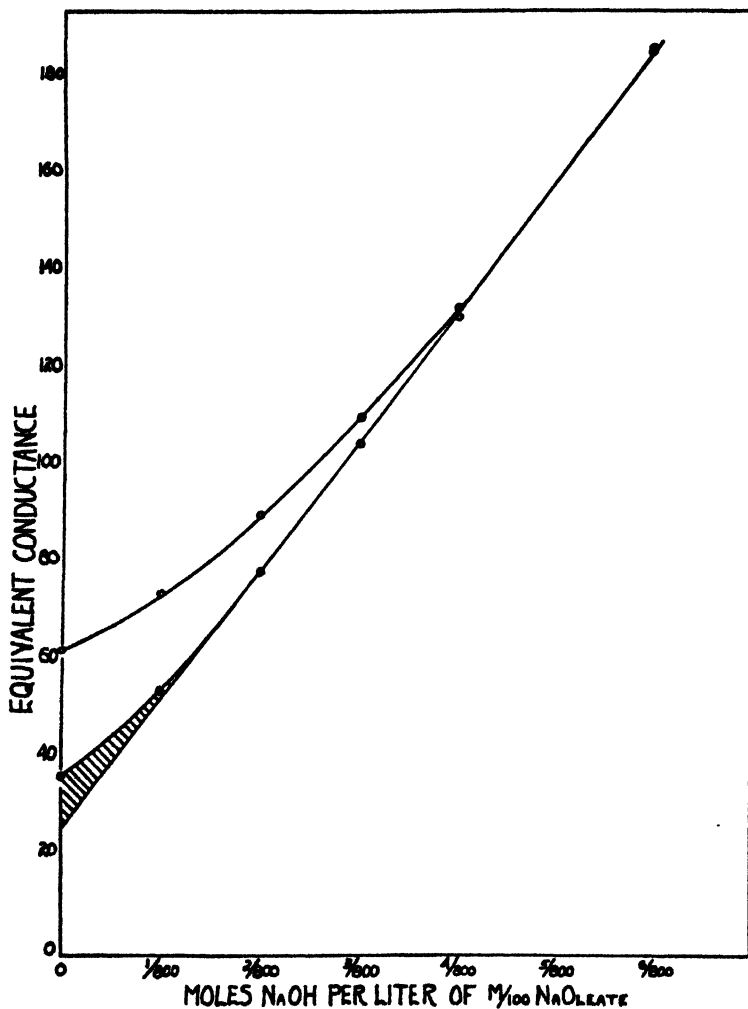


FIG. 3. The effect of sodium hydroxide on the increment of conductance due to *m*-xylene

surface pressures are exerted by acid sodium oleate. It follows then, that the surface pressure of a sodium oleate solution which impinges on its vapor has a very limited value when that datum is applied to the liquid-liquid interface between that same sodium oleate solution and an oil phase.

Owing to the fact that acid sodium oleate exerts the greater surface pressure, together with the fact that the hydrocarbon phase increases the quantity of it by selective adsorption and the resultant hydrolysis, the surface pressure of solute for a given sodium oleate solution in contact with an oil phase can exceed the surface pressure which obtains when the same solution impinges on its vapor.

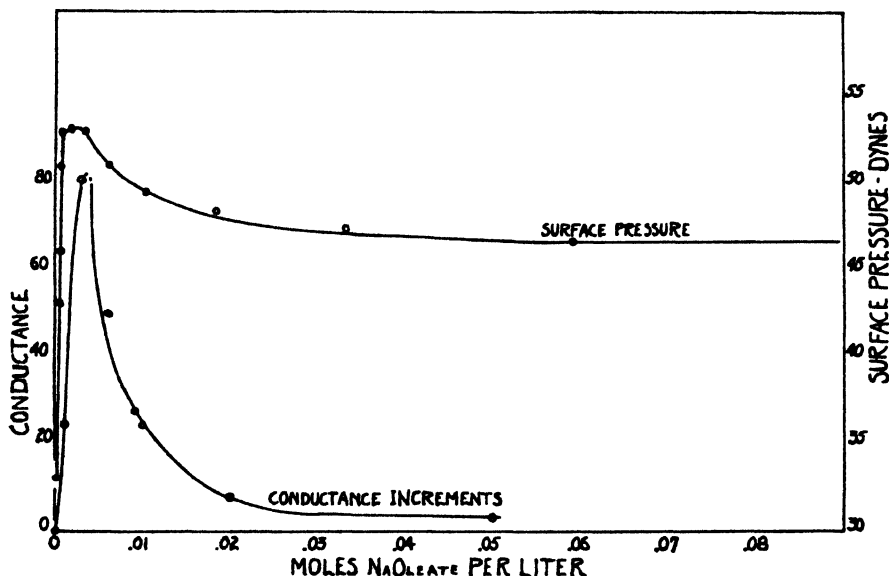


FIG. 4. A comparison of surface pressures with *m*-xylene conductance increments at different concentrations

CONCLUSIONS

The failure of Gibbs' equation must be attributed at least in part to a lack of knowledge of the processes involved. The inflexion points and negative slopes in the surface pressure-concentration relationship for sodium oleate are probably due to changes in the solute. If the concentration function were differentiated and each of the various forms of aggregates considered as a separate solute with individualistic properties, negative values of Γ would probably not arise.

Moreover, it seems that changes in the structure of surfaces not covered by the theory of orientation take place during and as a result of adsorption. There is probably a molecular re-orientation in the surface configuration of some oils at the plane of contact. As a consequence free and potential surface energies of the interface are altered. These changes must be included in Gibbs' equation.

The selective adsorption of acid sodium oleate by hydrocarbon oils alters

the surface pressure by an amount not predictable from surface tension measurements. The characteristics of the oil phase must be considered.

Relative sorption potentials, which should be useful data in the quantization of emulsions, are tabulated.

Some evidence in support of the idea that colloids involve potential energy changes has been given. In the case of sodium oleate and hydrocarbon oils free interfacial energy is stored in the cleavage of water.

The author is indebted to Dr. Paul Serex, whose sustained interest was invaluable to the progress of the work.

REFERENCES

- (1) Assoc. Official Agr. Chem.: *Methods of Analysis*, 3rd edition, p. 28. Washington, D. C. (1930).
- (2) COFMAN, V.: *Chem. Rev.* **4**, 1-49 (1927).
- (3) DU NOÛY, P. L.: *Surface Equilibria*, American Chemical Society Monograph. The Chemical Catalog Co., Inc., New York (1926).
- (4) HARKINS, W. D.: in *Alexander's Colloid Chemistry*, Vol. 1, p. 192. The Chemical Catalog Co., Inc., New York (1926).
- (5) HARKINS, W. D., CLARK, G. L., AND ROBERTS, L. E.: *J. Am. Chem. Soc.* **42**, 700 (1920).
- (6) HARKINS, W. D., DAVIES, E. C. H., AND CLARK, G. L.: *J. Am. Chem. Soc.* **39**, 584 (1917).
- (7) JOHLIN, J. M.: *J. Biol. Chem.* **84**, 543 (1929).
- (8) JOHLIN, J. M.: Private communication.
- (9) LANGMUIR, I.: *J. Am. Chem. Soc.* **39**, 1848 (1917).
- (10) LEWIS, W. C. McC.: *Phil. Mag.* **15**, 499 (1908).
- (11) McBAIN, J. W.: *Sorption of Gases and Vapours*, p. 8. Routledge & Sons, London (1932).
- (12) McBAIN, J. W.: *J. Soc. Chem. Ind.* **37**, 249T (1918).
- (13) McBAIN, J. W., AND HAY: *International Critical Tables*, Vol. V, p. 459. McGraw-Hill Book Co., New York (1929).
- (14) McBAIN, J. W., AND JENKINS, W. J.: *J. Chem. Soc.* **121**, 2325 (1922).
- (15) NICKERSON, R. F., AND SEREX, P.: *J. Phys. Chem.* **36**, 1585 (1932).
- (16) PENNYCUICK, S. W.: *J. Am. Chem. Soc.* **52**, 4621 (1930).
- (17) WALKER, E. E.: *J. Chem. Soc.* **119**, 1521 (1921).

NEW BOOKS

Optical Rotatory Power. By T. MARTIN LOWRY. 21.5 x 13.5 cm.; xiii + 483 pp. London: Longmans, Green and Co., 1935. Price: 30/- net.

It would require more space than is available to enumerate all the subjects which Professor Lowry deals with in this book, and it must suffice to say that in addition to an outline of the historical development of each theme, he gives valuable details of most of the apparatus used in polarimetric work, and a comprehensive treatment of the main problems at present under discussion, especially those to which his own investigations have been directed, or are related. Mostly the treatment is adequate, but in a number of cases it is incomplete, work quite relevant to the question dealt with being ignored; and it may be noticed that the diagram on p. 330 really represents the behavior not of nicotine but of ethyl tartrate (see *Z. physik. Chem.* **60**, 652 (1907)), whilst in the diagram on p. 154, the curve of ellipticities ought to be inverted (*J. phys.* [3] **7**, 84 (1898)).

In the theoretical parts of the book, the treatment is speculative, and often unsatisfactory from a logical point of view. Thus since quartz, and tartaric acid in solution, exhibit anomalous rotation dispersion, and the phenomenon in the latter case is attributed to the existence of dynamic isomers, it might be expected, by parity of reasoning, that quartz ought also to consist of several dynamic isomerides, a logical conclusion which there is, however, some reluctance to adopt.

This modern tendency towards deductive reasoning seems more than a little premature in regard to optical activity, considering that the very outlines of the subject have not yet been satisfactorily investigated, even in a qualitative sense. There is in fact, on account of the remarkable sensitiveness of the phenomena in question to various external and internal factors, hardly any subject which so little lends itself to such treatment. Nevertheless, Professor Lowry's book, representing as it does the attitude of a large school of investigators, will quickly become, on that account, as well as by its many valuable qualities, indispensable to workers in this field.

T. S. PATTERSON.

Colloid Symposium Monograph. Papers presented at the Eleventh Symposium on Colloid Chemistry, Madison, Wisconsin, June, 1934. Edited by H. B. Weiser. Baltimore: The Williams & Wilkins Company, 1935.

The Colloid Symposium since its birth has afforded an open forum where the somewhat artificial distinctions separating chemistry, physics, and physiology can be disregarded. Also it has been generally possible to achieve an elasticity of discussion not usual under the alarm-clock and stop-watch ridden sessions of major conventions. The publication of its proceedings as an annual monograph is generally justified, more particularly when as in the present volume one finds a feature subject rallying to it a number of papers. In this case the feature was cellulose. A sort of snails' race between colloid and cellulose chemists as to which should be the last to take notice of the other appears ended. In this collection the paper by W. D. Bancroft and J. B. Calkin entitled "Adsorption of Caustic Soda by Cellulose" does not appear to contain much new over their papers in *Textile Research*, but sums up clearly their evidence and arguments against any stoichiometric combination.

E. O. Krämer and W. D. Lansing contribute a valuable review of methods and data available for determining molecular weights of cellulose and its derivatives; S. E. Sheppard and P. T. Newsome a comparison of the properties of the cellulose (tri)-esters of the homologous fatty acids. The papers of A. Stamm and collaborators on the diffusion and sorption of water in wood and cellulose are rich in data and suggestive in argument. Papers on adsorption deal with both the experimental side and the theoretical—an interesting example of the latter being a critique by G. E. Cunningham of the Langmuir equation for the adsorption isotherm, and a proposed substitute. Several papers deal with electrokinetics in various applications. A technical paper by F. L. Browne on the behavior of paint as affected by gel changes of the vehicle, and a semi-technical one by W. D. Bancroft and P. H. Miller on cold vulcanization should be mentioned. The latter is remarkable as admitting that data which can be represented by a smooth adsorption curve may actually derive from stoichiometric combination.

S. E. SHEPPARD.

Orthohydrogen, Parahydrogen and Heavy Hydrogen. By ADALBERT FARKAS. 14.5 x 22 cm.; xiv + 215 pp. Cambridge: The University Press. New York: The Macmillan Company, 1935. Price: \$3.50.

This important addition to the Cambridge Series of Physical Chemistry will be welcomed by all investigators who are interested in hydrogen. The book is timely and is especially valuable because it combines the different phases of the subject in one volume. It is divided into two parts. Part I is devoted to ortho- and parahydrogen and its chapters are as follows: I. The Discovery of Orthohydrogen and Parahydrogen; II, Theory; III, The Properties of the Hydrogen Modifications; IV, The Kinetics of the Ortho-parahydrogen Conversion; V, Applications; VI, Ortho and Para Systems in other Molecules. Part II discusses heavy hydrogen in chapters entitled as follows: I, The Discovery of Heavy Hydrogen; II, The Preparation and Determination of Heavy Hydrogen; III, The Properties of Heavy Hydrogen; IV, The Chemistry of Heavy Hydrogen (1. Equilibria, 2. Kinetics).

The author, who personally has contributed much to the development of our knowledge of the subject, amply fulfills the purpose for which the book was written. This can best be stated as the author does when he says, "the purpose of this book is to describe the preparation, properties and chemical behavior of these different kinds of the same element and to illustrate how the investigations connected with this subject have contributed to the solution of some chemical and physical problems." The author gives a very complete review of the theoretical as well as the experimental work which has been completed since the discovery of ortho- and para-hydrogen in 1929. There is not much to be said in criticism of the book, for any lack of completeness must be attributed to the present state of development of the subject and not to omissions on the part of the author. Part I is therefore more complete than Part II. The combination of the theoretical with the experimental work seemed to the reviewer to be particularly well done. The book is heartily recommended to advanced students in physical chemistry as well as to those who are working in the field.

L. H. REYERSON.

The Principles of Experimental and Theoretical Electrochemistry. By MALCOLM DOLE. xiii + 549 pp. New York: McGraw-Hill Book Co., Inc., 1935. Price: \$5.00.

This is one of the most valuable books written on the subject of electrochemistry. During recent years the field has broadened so rapidly and new material, both experimental and theoretical, has appeared in such amounts that students have been

unable to keep up-to-date by reading original publications. In this book the author has analyzed most of the recent work and organized it and condensed it in a masterly manner. It is primarily a reference book, though it might be used as a text in a graduate course or, more especially, a seminar.

Several topics which are entirely omitted or briefly mentioned in other texts are given extensive treatment. Among these are: the Wien effect and Debye frequency effect, 11 pages; dielectric constants and electric moments, 35 pages; molecular rays, 27 pages; phase-boundary and semipermeable-membrane potentials, 20 pages; and the glass electrode, 16 pages. Especially interesting is the chapter entitled "Quantum Mechanics and Electrochemistry."

The author assumes a pronounced modern point of view. There are nearly seven hundred literature references, of which more than five hundred are to articles that have appeared during the last ten years, and more than three hundred since 1930.

The book is unusually free from errors. It is written in a clear, understandable style. Complex mathematical derivations have been omitted, though ample references are given to original sources for those who wish to follow through such derivations. Care is taken, however, to point out the assumptions involved in the mathematical developments, so that the reader may understand the limitations of applications of the final simple expressions included in the text. There are many curves and figures and many tables of data that assist the reader materially in following the discussions. One might be misled by the term "experimental" in the title of the book. It is in no sense a laboratory manual, but the experimental side of each topic is emphasized and actual data are extensively used in the discussion of theories.

Naturally there are several points about such a book that conflict with the views of each individual reader. The reviewer regrets that the author did not see fit to use some of the conventions and methods of attack that have become so generally accepted by the authors of the most popular texts in physical chemistry in the discussion of thermodynamics and electromotive force. Several instances might be mentioned where exceedingly elementary material is introduced that tends to detract from the high tone of the book as a whole. Among such topics may be mentioned the following: series and parallel circuits, the electrolysis of simple substances, and the Faraday and the coulometer, presented between pp. 29 and 33; the direct-current Wheatstone bridge, pp. 42-3; the voltmeter, potentiometers of the Pogendorff type, indicating devices (the moving-coil galvanometer), pp. 211-5; standard cells, and some useful electrodes, pp. 220-5. The material presented on these pages is found in the most elementary texts of physics and physical chemistry and must be familiar to any person interested in this book. And yet the subject of conductometric titrations, which has received such extensive development during the last few years that H. T. S. Britton published a book on the subject in 1934, is given only one page.

On the whole the book represents a difficult task remarkably well done. No person interested in electrochemistry or the theories of electrolytic solutions can afford to be without it.

ALFRED L. FERGUSON.

Electrons (+ and -), Protons, Neutrons and Cosmic Rays. By ROBERT A. MILLIKAN. 490 pp. Chicago: The University of Chicago Press, 1935. Price: \$3.50.

As the author explains in the preface, the present book is a direct outgrowth of the volume entitled *The Electron* published in 1917 (University of Chicago Press), which was revised in 1924 and further expanded when he delivered the Messenger Lectures at Cornell University.

Besides the small amount of revision necessary in the earlier parts, six entirely new chapters have been added on waves and particles, discovery and origin of cosmic rays, the spinning electron, the positron, the neutron and the transmutation of elements, and the nature of cosmic rays.

The name of the author is intimately associated with most of these new fields. The positron was discovered in his laboratory. He has been one of the leaders in the investigation of cosmic rays. The treatment as one might have expected is interesting, thorough and authoritative.

In the section on the divisibility of the electron the conclusion is reached that there is up to the present no evidence whatsoever of a sub-electron.

The work is splendidly illustrated with figures and photographs of cloud tracks and of apparatus.

S. C. LIND.

Absolute thermische Daten und Gleichgewichtskonstante. By R. DOCKEAL (in collaboration with H. Pitsch). 23 x 15 cm.; 69 pp.; three diagrams in pocket. Vienna: Julius Springer, 1935. Price: 6.60 RM.

This book contains a summary of the thermodynamic equations used in the calculation of energies, entropies, and free energies of substances, with data for hydrogen, oxygen, nitrogen, carbon monoxide, carbon, water, carbon dioxide, methane, and benzene given in tables and curves. These data are applied to the determination of equilibrium constants of some reactions of technical interest. The evaluation of equilibrium constants in dissociation reactions is then considered, the tables provided furnishing the values when the degree of dissociation is known. Since the data, particularly the specific heats of gases, are only very approximate, the results are in general more suitable for application in industrial conditions than in the research laboratory. The symbols used are not those employed in England or America and are printed in Gothic type. Within its limitations the book is likely to be very useful and the authors appear to have taken pains in selecting the data. It should be particularly useful in works laboratories where problems of the type it deals with must frequently call for solution.

J. R. PARTINGTON.

THE THERMODYNAMIC PROPERTIES OF CADMIUM SULFATE IN WATER-ETHYL ALCOHOL SOLUTIONS

VICTOR K. LAMER AND ERWIN L. CARPENTER

Department of Chemistry, Columbia University, New York

Received August 20, 1935

INTRODUCTION

The purpose of this research was to investigate how the partial free energy, heat content, and heat capacity of a typical bivalent electrolyte, cadmium sulfate, are affected on lowering the dielectric constant by the addition of ethyl alcohol to its aqueous solution.

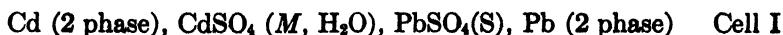
It can be demonstrated (7, 20) that the electric free energy of an ion can be computed from the work of reversibly charging the ion from a reference potential to its actual potential ψ . The latter is composed of two parts: first, a part ψ_0 which exists in the absence of any surrounding ions and arises by virtue of its own charge; and second, a part ψ^* which arises from the unequal distribution of the surrounding ions as interpreted by the Debye-Hückel interaction theory. The interaction effect depends upon $D^{-3/2}$ as a limiting first approximation, and upon a parameter a which represents in terms of the model the distance of closest approach of the ions. The interaction effect can be eliminated exactly when the experimental results at finite concentration permit of an unequivocal extrapolation to infinite dilution.

The potential, ψ_0 , which generally is of greater magnitude, should, according to Born (3), vary inversely with the radius of the ion and the dielectric constant. Born's equation for the solvent effect assumes the same simple model, namely, that the ions may be represented by spheres of radius r_i , and the medium by a continuous dielectric having the macroscopic value D . All chemical processes of solvation are ignored.

One aspect of this investigation was to ascertain in how far this simple model can account for the experimental results obtained with a bi-bivalent salt, where the electric effects are of greater magnitude than with a uni-univalent salt, by comparing the radii of the ions as computed from the Born equation with the value a as given by the interaction theory. Although a number of investigators (6, 10, 11, 19, 23) have utilized galvanic cells to study medium effects in terms of the free energy of transfer of electrolytes, no systematic investigation of temperature coefficients in non-aqueous solvents has been made. Such studies are of importance since

they furnish accurate data for the calculation of changes in the heat content and heat capacity of the cell process from which the thermal properties of the electrolyte can be readily obtained. Owing to the highly reproducible behavior of cadmium amalgam and mercurous sulfate electrodes, cells containing these electrodes are most suitable for attacking this problem.

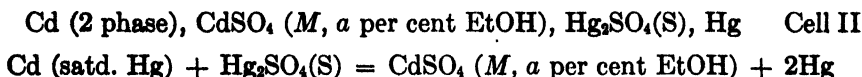
Since the requisite data for aqueous cadmium sulfate are available from the studies of LaMer and Parks (17) on the amalgam cell:



for which the cell process is:

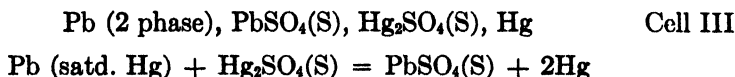


we first investigated this cell by replacing the water progressively with ethyl alcohol. Equilibrium, however, was attained so slowly in the presence of alcohol that cell I was abandoned in favor of the amalgam cell using mercurous sulfate instead of lead sulfate:

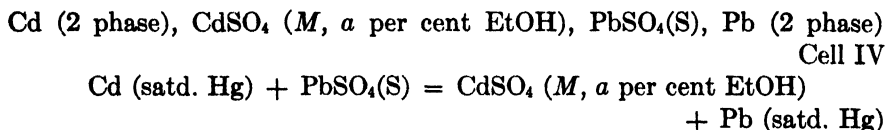


The limited success which the mercurous sulfate electrode has achieved in aqueous solution is due primarily to the uncertainty arising from the relatively large corrections for its solubility, which must be applied when the concentration of the more soluble sulfate (cadmium sulfate) is less than 0.005 *M*. Fortunately, the solubility of mercurous sulfate is greatly reduced by the addition of alcohol. In 33.3 weight per cent ethyl alcohol, using Hulett's method (14) of precipitating the mercury as chloride by the addition of hydrochloric acid, we find $S_{\text{Hg}_2\text{SO}_4} = 1.8 \times 10^{-5}$ moles per liter. The same value was obtained in experiments in which the alcohol was first evaporated and the chloride precipitated from aqueous solution. The solubility product of mercurous sulfate in 33 weight per cent alcohol is consequently so small that no correction for sulfate ion is necessary in calculating the observed normal potentials E^o , even for concentrations as low as 0.001 *M* cadmium sulfate. Furthermore, cell II yielded highly reproducible potentials and hence is well suited for our purpose, even though its use is limited to rather narrow ranges of concentration as a result of the decreased solubility of both cadmium sulfate and mercurous sulfate. In 15 per cent ethyl alcohol the lower limit for precise work is 0.01 *M* cadmium sulfate; in 33 per cent ethyl alcohol the limits are 0.001 *M* extending to saturation (about 0.01 *M*); above 33 per cent ethyl alcohol the internal resistance of the cell is so high that 0.01 *M* is the practical lower limit; above 50 per cent alcohol cadmium sulfate becomes too insoluble for precise measurements.

To compare the results in water using cell I with those in alcohol using cell II, it is necessary to know the thermal properties of cell III:



Subtracting cell III from cell II yields



of nitrogen in glass apparatus having an efficient fractionating column. The middle and last fractions were found to be aldehyde-free when tested with fuchsin-sulfite reagent as described by Woodman (26). The specific gravity of the alcohol was then taken at 25°C. The weight per cent of the alcohol was determined from the density.

Mercurous sulfate. Mercurous sulfate was prepared electrolytically by the Hulett method (15), in which purified mercury served as the anode and a platinum wire dipping into sulfuric acid of density 1.15 was the cathode. The product was gray, owing to the presence of finely divided mercury, which is a distinct advantage in checking any tendency of the mercurous ion to be oxidized to mercuric ion. Vosburgh and Eppley (25) have shown that samples of mercurous sulfate prepared by three different methods—the reduction of mercuric sulfate by mercury, direct current electrolysis, and the reaction of mercurous nitrate and sulfuric acid—give E.M.F.'s agreeing within 0.01 mv. Åkerlöf (1) also obtained satisfactory results with mercurous sulfate prepared electrolytically in his study on the alkali sulfates. The mercurous sulfate was stored in the dark under 2 molal sulfuric acid in a Nonsol bottle.

EXPERIMENTAL METHOD

The cell vessel used for cells I and II was the same as that developed by Cowperthwaite and LaMer (5) for their study of zinc sulfate. This type of cell vessel permits the entire filling operation to be carried out in an atmosphere of nitrogen, and the cell can then be sealed off under mercury. The reader should consult their paper for the diagram and details of manipulation.

The type of cell vessel used by LaMer and Parks was found to be more suitable for cell III, where two solids are involved. Their cell vessel is composed of six electrodes divided by three large bore stop-cocks into two groups of three each. On one side three similar lead-lead sulfate electrodes and on the other side three similar mercurous sulfate-mercury electrodes are set up. This type of vessel has the particular advantage that measurements to check the constancy and reproducibility of each leg of the three electrodes forming the one half-cell as well as the measurements of the three total cells can be made without disturbing the contents or the vacuum.

EXPERIMENTAL DATA

To test the reproducibility and freedom from hysteresis of cell II in alcohol solutions, three sets of five cells each were made up on different days. The concentrations of cadmium sulfate and ethyl alcohol were respectively 0.01 *M* and 33.3 per cent. The average deviation at 25°C. was ± 0.0064 mv. For two of these sets, the readings were taken at different temperatures in the order: 25°, 30°, 20°, 15°, 10°, 0°, 10°, 20°, 25°.

and 30°C. The combined averages of the values obtained at descending and ascending temperatures of the two sets never had an average deviation greater than ± 0.02 mv.; usually much less. Cell II is not only reproducible but it exhibits little, if any, temperature hysteresis.

Henderson and Mellon (12), using both a saturated and an unsaturated solution of sodium sulfate as the conducting medium, found that cell III

TABLE 1
Observed E.M.F. of cell III

TEMPERATURE $t^{\circ}\text{C.}$	NO OF CELLS MEASURED	$E = E' = E''$
0 0	3	0 96051
12 5	3	0 96262
25 0	6	0 96471
37 5	3	0 96680
50 0	3	0 96891

TABLE 2
Values of E for 0.01 M cadmium sulfate

$t^{\circ}\text{C.}$	E (I) (H_2O)	E (II) (33.3 PER CENT ALCOHOL)	E (II) (50 PER CENT ALCOHOL)	E (IV) (33.3 PER CENT ALCOHOL)	E (IV) (50 PER CENT ALCOHOL)
0 0	0 14651	1 04526	1 02425	0 08475	0 06374
10 0	0 14720	1 04780	1 02596	0 08561	0 06377
15 0	(0 14673)	1 04870	1 02659	0 08567	0 06356
20 0	0 14588	1 04942	1 02707	0 08555	0 06320
25 0	(0 14476)	1 04997	1 02744	0 08526	0 06273
30 0	0 14346	1 05032	1 02774	0 08477	0 06219

$t^{\circ}\text{C.}$	E' (I) (H_2O)	E' (II) (33.3 PER CENT ALCOHOL)	E' (II) (50 PER CENT ALCOHOL)	E' (IV) (33.3 PER CENT ALCOHOL)	E' (IV) (50 PER CENT ALCOHOL)
0 0	0 03812	0 93687	0 91586	-0 02364	-0.04465
10 0	0 03485	0 93545	0.91361	-0 02674	-0 04858
15 0	(0 03239)	0 93436	0 91225	-0 02867	-0.05078
20 0	0 02956	0 93310	0 91075	-0 03077	-0 05312
25 0	(0 02645)	0 93166	0 90913	-0 03305	-0 05558
30 0	0 02317	0 93003	0 90745	-0 03552	-0 05810

* () interpolated values.

gave an E.M.F. of 0.96466 at 25°C. They also demonstrated that the E.M.F. was independent of the conducting medium by using saturated and unsaturated solutions of nickel, zinc, manganese, and cobalt sulfates in place of sodium sulfate.

In table 1 are given our results for cell III over a wider temperature interval, using as solvents 0.33 *M* sodium sulfate and 0.002 *M* sulfuric acid (to prevent hydrolysis in water), and 0.01 *M* sodium sulfate in 33.3 per

cent ethyl alcohol. The measurements of the two sets agreed within ± 0.02 mv. and checked Henderson and Mellon's value at 25°C. to 0.05 mv.

In table 2 are recorded the observed values of E for the respective cells for 0.01 M cadmium sulfate in the solvents water (column 2), and 33.3 per cent and 50 per cent ethyl alcohol (columns 3 and 4) at various temperatures. Each value represents the average of at least five cells; the average deviation was never greater than ± 0.02 mv., and in many cases only ± 0.01 mv. The values for the cell process IV, obtained by subtracting the temperature-interpolated values of E (III) from E (II), are given for purposes of direct comparison with cell I with which they are equivalent except for the presence of alcohol.

In table 3 are given the observed values for cell II for different concentrations of cadmium sulfate in 33 per cent ethyl alcohol at 25°C. Each value represents the average of at least five cells; the average deviation was

TABLE 3

E for cells I, II, and IV as function of concentration of cadmium sulfate and per cent of alcohol at 25°C.

<i>M</i>	0 PER CENT ALCOHOL	33 PER CENT ALCOHOL	
	I	II	IV
0.01	0.14476	1 04997	0 08526
0.008	0.14877	1 05249	0.08778
0.006	0.15404	1 05577	0.09106
0.004	0.16158	1 06017	0.09546
0.002	0.17424	1.06686	0.10215
0.001	0.18840	1 07386	0.10915

15 per cent alcohol at 0.01 M ; E (II) = 1.07908 ; E (IV) = 0.11437 .

never greater than ± 0.04 mv. The values for cell I in water were taken from a large scale graph of LaMer and Parks' (17) $E^{0'}$ values after they had been interpolated to 25°C. using an equation of the third degree in t .

THEORETICAL

When a mole of salt is transferred from an aqueous solution of dielectric constant D_2 to an alcoholic solution of dielectric D_1 , the reversible work of transfer arises from two sources. The excess electrical free energy, which the ions possess by virtue of their unequal distribution as interpreted by the Debye-Hückel interaction theory, changes somewhat with the change in the dielectric constant. Secondly, the individual ions of radius r_i possess a greater electrical free energy in the medium of low dielectric constant by virtue of the greater amount of work which is necessary to charge reversibly these ions for such a medium. Born's equation for this solvent medium effect is

$$\Delta \bar{F}_0 = \frac{(ze)^2 N}{2} \left(\frac{1}{D_1} - \frac{1}{D_2} \right) \left(\frac{1}{r_+} + \frac{1}{r_-} \right) \quad (1)$$

$\Delta \bar{F}_0$ is the free energy change at infinite dilution, where the effects of interaction are absent.¹

The activity coefficient often is a more convenient quantity to use in the numerical treatment of experimental data than is the free energy. Any activity coefficient whose standard state of reference is taken as unity for infinite dilution in pure water will be designated by the symbol f . When the activity coefficient is referred to the standard state of infinite dilution in a particular water-alcohol medium, an asterisk will be used (f^*). A subscript zero indicates that the concentration of electrolyte is zero, and when the medium is pure water, a superscript zero will be used (f^0 ; $f_0^0 = 1$, etc.). All concentrations of cadmium sulfate are expressed in moles per kilogram of solvent; the concentration of alcohol in weight per cent.

TABLE 4
"Total medium effect" $\log f/f^0$ for cadmium sulfate at 25°C.

WEIGHT PER CENT ETHYL ALCOHOL	D	0.01 M	0.008 M	0.006 M
15.0	70.14	0.5138		
33.3	59.16	1.0059	1.0311	1.0647
50.0	48.93	1.3867		
WEIGHT PER CENT ETHYL ALCOHOL	D	0.004 M	0.002 M	0.001 M
33.3	59.16	1.1178	1.2187	1.3398

In terms of these definitions, the total medium effect is $\log f/f^0$ and is composed of two parts, the solvent effect $= \log f_0/f_0^0 = \log f_0$, since $f_0^0 = 1$, plus the interaction medium effect $\log f^*/f^0$. Thus

$$\log f/f^0 = \log f_0 + \log f/f^0 \quad (2)$$

Owen (21) uses the terms "primary" and "secondary" medium effects, but we prefer the more descriptive terms "solvent" and "interaction." They are obviously related to the potentials ψ_0 and ψ^* mentioned in the introduction.

The total medium effect is obtained directly from the E.M.F. of the double cell I-IV by the relation

$$E = E(\text{IV}) - E(\text{I}) = 0.05915 \log f/f^0 \quad (3)$$

¹ Ze is the charge on the ion, N is Avogadro's number, and r_+ and r_- are the radii of the cation and anion.

The results are given in table 4 for the concentrations of cadmium sulfate and alcohol studied.

Calculation of the solvent medium effect and the interaction coefficient f^* requires a knowledge of E^0 for cell II in alcohol. In figure 1 we have plotted the values of E^0 ; defined as

$$E^0 = E + \frac{\nu RT}{n\mathfrak{F}} \ln M; \quad E^0 = E^0 - \frac{\nu RT}{n\mathfrak{F}} \ln f^* \quad (\nu = n = 2) \quad (4)$$

against the square root of the molality for 33.3 per cent ethyl alcohol. The data obviously do not approach the limiting slope of the Debye-

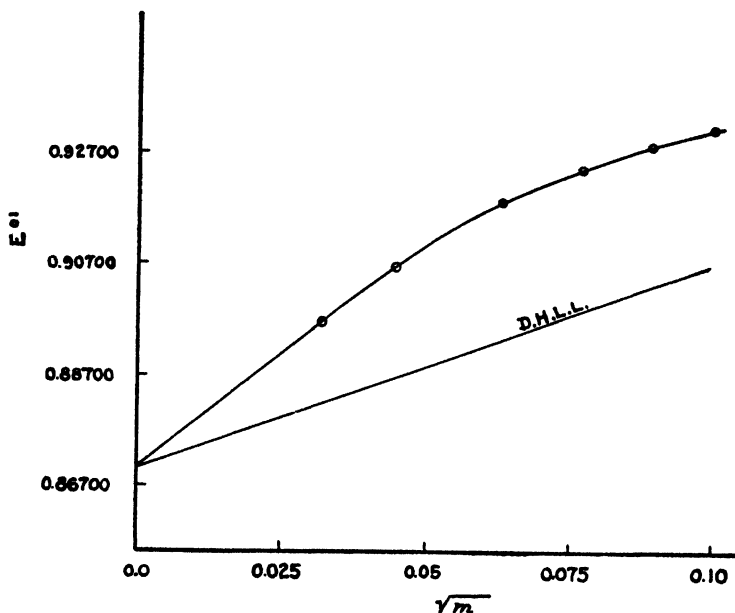


FIG. 1

Hückel theory at concentrations as low as 0.001 M . This behavior has been observed (4, 9) previously for the solubility data of salts in methyl and ethyl alcohol-water mixtures.

Fortunately, a precise value of E^0 is not necessary, since a comparatively large error in $\log f^*$ results in only a small error in $\log f_0$, f^* never being greater than 1 per cent of f_0 . In table 5 we give the calculation of E^0 using the Gronwall, LaMer, and Sandved (8) equation for the activity in equation 4 for $a = 2.92$ A.U., which proved to give the best fit.

It will be noticed that the individual values fluctuate more from the average than they do for cadmium sulfate in water solution. This is due to the fact that the higher terms do not converge rapidly in the case of the

alcohol solution ($D = 59.16$), whereas they do converge with sufficient rapidity in the case of water ($D = 78.54$). LaMer and Parks obtained a constant E^0 when an ion size of 3.6 A.U. units was used. Whether the decrease in a from 3.6 A.U. in water to 2.92 A.U. in 33.3 per cent alcohol is real, or arises from insufficient convergence, or is due to theoretical weaknesses in the Debye-Hückel theory cannot be determined at present. It is gratifying that the E^0 calculated over the range from 0.01 M to 0.001 M , agrees within 0.16 mv. of the value obtained by the linear graphical extrapolation. We estimate that E^0 is known to ± 0.0005 volt, which fortunately introduces an uncertainty in the calculation of the solvent medium effect of only ± 0.5 per cent. Using the average value $E^0 = 0.87033$, the solvent medium effect for 33.3 per cent ethyl alcohol in the absence of any interaction effects equals 1.6246.

According to the Born equation, the solvent medium effect, $\log f_0$,

TABLE 5

Calculation of E^0 by the Gronwall, LaMer, and Sandved extension; $a = 2.92$ A.U.

CONCENTRATION	E^0	DEVIATION FROM MEAN
0 01	0 87075	0 00044
0 008	0 86994	-0 00047
0 006	0 86966	-0 00075
0 004	0 87006	-0 00035
0 002	0 87095	0 00054
0 001	0 87107	0 00065
Average	0 87041 \pm 0 0005	
Graphical extrapolation	0 87025	

should be proportional to the reciprocal of the dielectric constant of the solvent, a prediction which Åkerlöf (2) found to hold fairly well for sodium, potassium, lithium, and hydrogen chlorides up to 80 per cent methyl alcohol in water ($D = 42.3$). The dotted line in figure 2 has been drawn on this assumption. The distance from any point on the solid line to the dotted line at the same value of $1/D$ is equal to the interaction medium effect, which, it will be noted, rapidly becomes of greater importance as the dielectric constant decreases.

From the slope of the dotted line we calculate that

$$\frac{2}{r} = \left(\frac{1}{r_+} + \frac{1}{r_-} \right)$$

corresponds to a value of $r = 1.24$ A.U. If the ions are spherical and no forces of deformation intrude, $a = 2r = 2.48$ A.U. The disagreement with $a = 2.92$ A.U., calculated from the Gronwall, LaMer, and Sandved

form of the interaction theory, while outside experimental error, is not serious considering the highly simplified character of the model which completely neglects any influence of solvation.

In column 2 of table 6 are given the values of f^* , the interaction activity coefficient for cadmium sulfate in 33 per cent ethyl alcohol and referred to

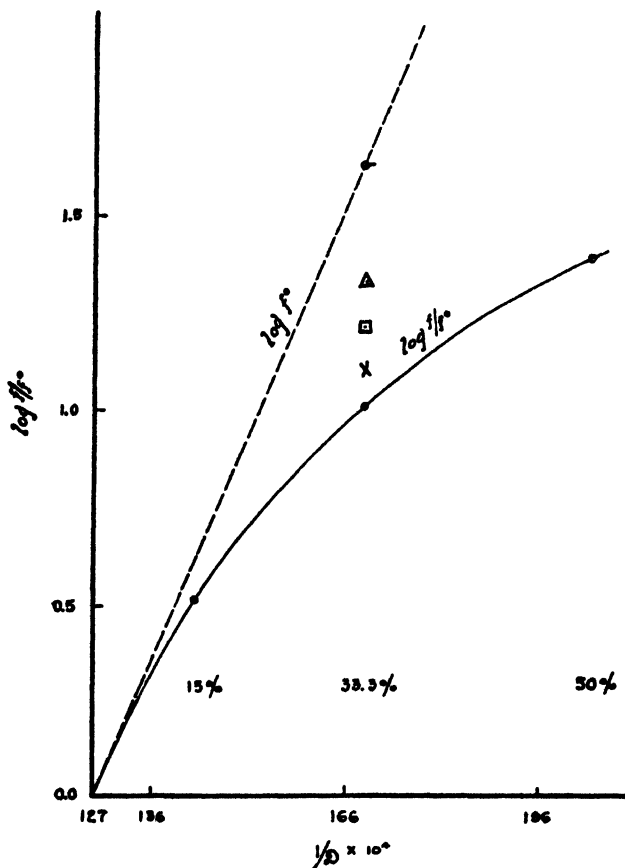


FIG. 2

○, 0.000 M; △, 0.001 M; □, 0.002 M; ×, 0.004 M; ⊙, 0.010 M

unity at infinite dilution in this solvent and in column 3, f^0 , the corresponding activity coefficients in aqueous solution. The last column gives the interaction medium effect $\log f^*/f^0$.

The decrease in molal heat content ($-\Delta H$) and the increase in molal heat capacity (ΔC_p) are related to the E.M.F. of the cell process by the relations:

$$-\Delta H = n\mathfrak{F} \left[E - T \left(\frac{\partial E}{\partial T} \right)_p \right] \quad (5)$$

$$\Delta C_p = \left(\frac{\partial \Delta H}{\partial T} \right)_p = n\mathfrak{F} T \left(\frac{\partial^2 E}{\partial T^2} \right)_p \quad (6)$$

It can be shown that if $E^{0'}$ is plotted (17) against $1/T$ the slope of the curve at any point is a measure of the magnitude of $(-\Delta H)$ corresponding to the

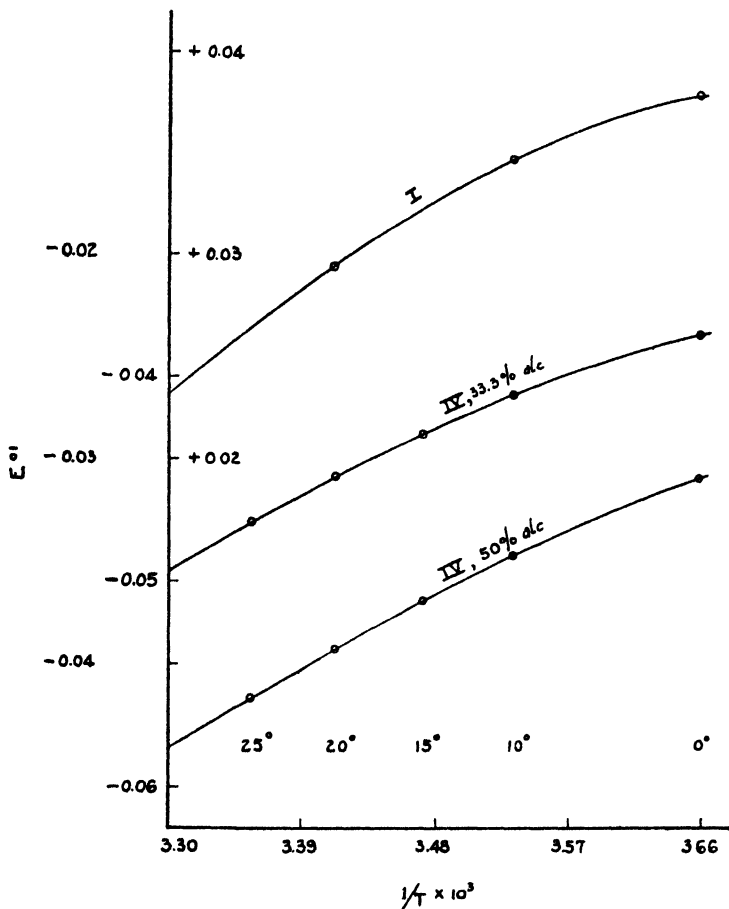


FIG. 3

Scale of ordinates reading from left to right refers to cell IV (50 per cent alcohol), cell IV (33 per cent alcohol), and cell I (water).

temperature and composition of the solvent at that point. Similarly, the curvature is a measure of the value of ΔC_p for the cell process.

If E^0/T is plotted against $1/T$, the slope is directly related to $-\Delta H$ and the curvature directly to ΔC_p .

The values of E^0 for cells I and IV are thus plotted in figure 3, from which it is evident that with increasing alcohol content $-\Delta H$ decreases and ΔC_p becomes less negative, i.e., it increases.

To facilitate the numerical computation of these quantities we have expressed E for the different cell processes at 0.01 M cadmium sulfate as polynomials of the third degree in terms of $t^\circ\text{C}.$:

$$E = A + Bt + Ct^2 + Dt^3 \quad (7)$$

using the experimental values of the E.M.F. at 0° , 10° , 20° , and $30^\circ\text{C}.$ To test the reliability of the derived equation, the computed values of E for

TABLE 6
Interaction activity coefficients of cadmium sulfate at $25^\circ\text{C}.$

M	f^0 (33 PER CENT EtOH)	f^0 (H_2O)	$-\log f^0/f^0$
0.001	0.363	0.698	0.285
0.002	0.238	0.606	0.406
0.004	0.154	0.496	0.507
0.006	0.122	0.443	0.560
0.008	0.104	0.408	0.594
0.010	0.092	0.382	0.619

TABLE 6a
Coefficients $\times 10^5$ for equations 10 and 11

CELL PROCESS	A	B	C	D
I (0 per cent, $M = 0.01$).....	14651	19.9833	-1.46	0.015167
III (Independent of solvent)....	96051	16.8000	0.0	0.0
IV (33.3 per cent, $M = 0.01$)....	8475	13.8667	-0.56	0.003333
IV (50 per cent, $M = 0.01$)....	6374	3.8333	-0.38	0.002667

the two temperatures, 15° and $25^\circ\text{C}.$, were compared with the experimental values. The calculated and experimental values checked in all cases within ± 0.02 mv. The empirical equation may accordingly be relied upon to give the correct derivatives within the limits of accuracy of the data. Such a check is not obtained if a second degree equation is employed. The coefficients of equation 7 are given in table 6a.

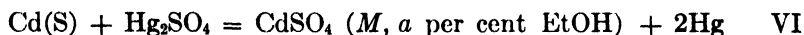
ΔH and ΔC_p , calculated by substituting the proper analytical expressions of the derivatives of equation 7 in equations 5 and 6 are given in table 7 for $15^\circ\text{C}.$, for which temperature the higher derivatives should be most reliable. Column 5 for $\frac{\partial \Delta C_p}{\partial T}$ is included to preserve consistency with the

experimental values of E at the various temperatures, but no claim is made for accuracy since this quantity depends upon the third derivative $\partial^3 E / \partial T^3$.

Since Parks and LaMer (22) have measured the E.M.F. and its temperature derivatives of the cell for which the process is



ΔH and ΔC_p for the process



were computed by the relation $\text{VI} = \text{II} + \text{V}$.

TABLE 7
Summary of results for 15°C. (288.1°K) in calories

PROCESS	PER CENT EtOH	— ΔH	ΔC_p	$\frac{\partial \Delta C_p}{\partial T}$
III $\text{Pb (satd.Hg)} + \text{Hg}_2\text{SO}_4(\text{S}) = \text{PbSO}_4 + 2\text{Hg}$		42,208	0	0
IV $\text{Cd (satd.Hg)} + \text{PbSO}_4 = \text{CdSO}_4 (0.01 M) + \text{Pb (satd.Hg)}$	0 0	8,577	—207	11 4
	33 3	4,045	—109	2 3
	50 0	3,670	—69	2 2
VI $\text{Cd(S)} + \text{Hg}_2\text{SO}_4(\text{S}) = \text{CdSO}_4(0.01 M) + 2\text{Hg}$	0.	56,041	—220	17 4
	33 3	51,509	—122	8 3
	50 0	51,134	—82	7 8
VII $\text{Cd(S)} + \text{PbSO}_4(\text{S}) = \text{CdSO}_4(0.01 M) + \text{Pb (satd.Hg)}$	0.	13,833	Same as process VI	
	33 3	9,301		
	50 0	8,926		

In a similar way the same quantities for process VII, involving solid cadmium instead of the two-phase amalgam, can be computed from the relation $\text{VII} = \text{IV} + \text{V}$.

HEAT CONTENTS AND HEAT CAPACITIES OF DILUTION

The values² for

$$\Delta \bar{H} = \bar{H}(0.01 M, a \text{ per cent EtOH}) - \bar{H}(0.01 M, \text{H}_2\text{O})$$

and

$$\Delta \bar{C}_p(0.01 M) = \bar{C}_p(0.01 M, a \text{ per cent EtOH}) - \bar{C}_p(0.01 M, \text{H}_2\text{O})$$

arising from the transfer of a mole of cadmium sulfate from a 0.01 molal solution in water to a 0.01 molal solution in 33.3 and 50 per cent ethyl

² The partial molal quantities, designated by the bar, always refer to the solute. The customary subscript 2 has been omitted as unnecessary in this paper.

alcohol are given in table 8 for the temperatures 10°, 15°, and 20°C. The values of \bar{L} (0.01 *M*) and \bar{c}_p (0.01 *M*) are tabulated for the different temperatures in table 9. \bar{L} is defined by the equation

$$\bar{L} = \bar{H} (0.01 \text{ } M, a \text{ per cent EtOH}) - \bar{H}^0 (M = 0, \text{H}_2\text{O})$$

$$\bar{c}_p = \Delta c_p (\text{VI}) + c_p(\text{Cd}) + c_p(\text{Hg}_2\text{SO}_4) - 2c_p(\text{Hg})$$

using the values as given in the International Critical Tables for solid cadmium, mercurous sulfate, and liquid mercury. The values for \bar{L} (0.01 *M*) and \bar{c}_p (0.01 *M*) for cadmium sulfate in water (22) are also listed for comparison. Table 9 shows that c_p (0.01 *M*) for cadmium sulfate is very nearly a linear function of the weight per cent of alcohol.

TABLE 8
Values of $\Delta\bar{H}$ and $\Delta\bar{c}_p$

a PER CENT EtOH	$\Delta\bar{H} = \bar{H} (0.01 \text{ } M, a \text{ PER CENT EtOH}) - \bar{H}^0 (0.01 \text{ } M, \text{H}_2\text{O})$			$\Delta\bar{c}_p = c_p (0.01 \text{ } M, a \text{ PER CENT EtOH}) - c_p (0.01 \text{ } M, \text{H}_2\text{O})$		
	10°C.	15°C.	20°C.	10°C.	15°C.	20°C.
33	3931	4532	4906	143	98	52
50	4073	4907	5446	185	138	89

TABLE 9
Values of \bar{L} and \bar{c}_p

a PER CENT EtOH	$\bar{L} = \bar{H} (0.01 \text{ } M, a \text{ PER CENT EtOH}) - \bar{H}^0 (M = 0, \text{H}_2\text{O}) \text{ FOR CdSO}_4$			$\bar{c}_p (0.01 \text{ } M, a \text{ PER CENT EtOH}) \text{ FOR CdSO}_4$		
	10°C.	15°C.	20°C.	10°C.	15°C.	20°C.
0.0	526	621	752	-280	-195	-106
33.3	4457	5153	5658	-137	-98	-54
50.0	4599	5528	6198	-95	-58	-17

In order to obtain an estimate of the probable error in these values, 0.02 mv., which was the average deviation of the experimental results, was added to or subtracted from the measurements, and new values calculated. In the case of the heat content, it was found that the maximum error was obtained if the 0.02 mv. was alternately added to and subtracted from the measurements. This amounted to ± 1.3 per cent (± 62 cal.). In the case of the heat capacity, the maximum error was obtained if the 0.02 mv. was added to the first measurement and subtracted from the third. This amounted to ± 2.4 per cent (± 2.6 cal. per degree). The probable error in \bar{L} may be twice as large as the error in $\Delta\bar{H}$ of transfer, since it involves the subtraction of one $\Delta\bar{H}$ from another. The error in \bar{c}_p may also be twice as large as the error in Δc_p , as it is necessary to add the change in the heat

capacity involved in the transfer of a mole of solid cadmium from the solid state to a two-phase amalgam to Δc_p from process II. The heat capacities of the solids, cadmium and mercurous sulfates, and that of liquid mercury are accurate to about 0.1 cal. per degree.

Henderson and Stegeman (13) measured the E.M.F. of cell III at 18°, 25°, and 30°C. From their empirical second-degree equation one would expect that Δc_p (III) = 10.5 cal. per degree. Although our measurements upon the same cell at 0°, 12.5°, 25°, 37.5°, and 50°C. yield a value of ΔH (III) at 18°C. which checks their value within 0.2 per cent (69 cal.), we find $\partial^2 E / \partial T^2$ (see table 7) to be equal to zero. Consequently, Δc_p (III) should be zero. This prediction can be checked, using the calorimetric heat capacity data for the respective solids given in International Critical Tables, Vol. V, pp. 85-97. The calorimetric data require Δc_p (III) equal to 0.1 cal. This agreement furnishes further evidence that the changes in heat capacity in chemical processes may be accurately calculated from precise E.M.F. measurements, provided the data extend over a wide range of temperature and an empirical equation of sufficient power for accurate representation is employed.

These data show that for 15°C. the molal heat of dilution in water of 0.01 *M* cadmium sulfate is 621 cal., whereas the heat effect involved in transferring one mole of cadmium sulfate at 0.01 molal from 33 per cent alcohol to water is 4532 cal., i.e., the thermal effect of interaction in water is about 12 per cent of that of transfer, which is essentially a pure solvent effect.

Perhaps the most striking result of this investigation is the almost linear increase (i.e., to less negative values) which the partial heat capacity of the salt undergoes on the addition of alcohol. The large negative values for \bar{c}_p which salts exhibit in water is ascribed by Zwicky (27) to compression of the solvent in the neighborhood of the ion and to a loss in degrees of freedom of the solvent as result of electrostriction. In a solvent of lower dipole moment such effects are less and hence a less negative value of \bar{c}_p is observed.

SUMMARY

1. E.M.F. measurements are reported for the cell:

Cd (two-phase amalgam), CdSO_4 (*M*, *a* per cent EtOH), $\text{Hg}_2\text{SO}_4(\text{S})$, Hg for *M* = 0.01 in 33.3 and 50 per cent ethyl alcohol at 0°, 10°, 15°, 20°, 25°, and 30°C.; as a function of *M* in 33.3 per cent alcohol at 25°C.; and for *M* = 0.01 in 15 per cent alcohol at 25°C.

The cell: Pb (two-phase amalgam), $\text{PbSO}_4(\text{S})$, $\text{Hg}_2\text{SO}_4(\text{S})$, Hg has been measured at 12.5°C.-intervals over the range 0° to 50°C.

2. The partial heat contents, and the partial heat capacities of cadmium sulfate have been calculated in the alcoholic solutions for comparison with the corresponding aqueous solutions.

3. The total medium effect for 0.01 molal cadmium sulfate in 15, 33.3, and 50 per cent alcohol, and the solvent and interaction medium effects in 33.3 per cent alcohol, have been evaluated. The results have been considered in the light of the Born transfer equation and the extended form of the Debye-Hückel interaction theory.

4. The value of r , the mean ionic radius of the cadmium and sulfate ions as calculated from the Born equation, is in fair agreement with the value of a , the distance of closest approach of two ions, calculated by means of the extended theory of Debye and Hückel.

REFERENCES

- (1) ÅKERLÖF: J. Am. Chem. Soc. **48**, 1160 (1926).
- (2) ÅKERLÖF: J. Am. Chem. Soc. **52**, 2353 (1930).
- (3) BORN: Physik. Z. **1**, 45 (1920).
- (4) BRÖNSTED, DELBANCO, AND VOLQUARTZ: Z. physik. Chem. **162A**, 128 (1932).
- (5) COWPERTHWAIT AND LAMER: J. Am. Chem. Soc. **53**, 4333 (1931).
- (6) DANNER: J. Am. Chem. Soc. **44**, 2832 (1922).
- (7) DEBYE: Physik. Z. **25**, 97 (1924).
- (8) GRONWALL, LAMER, AND SANDVED: Physik. Z. **29**, 358 (1928).
- (9) HANSEN AND WILLIAMS: J. Am. Chem. Soc. **52**, 2759 (1930).
- (10) HARDMAN AND LAPWORTH: J. Chem. Soc. **99**, 2242 (1911); **101**, 2249 (1912).
- (11) HARNED AND FLEYSHER: J. Am. Chem. Soc. **47**, 82 (1925).
- (12) HENDERSON AND MELLON: J. Am. Chem. Soc. **42**, 676 (1920).
- (13) HENDERSON AND STEGEMAN: J. Am. Chem. Soc. **40**, 84 (1918).
- (14) HULETT: Phys. Rev. **27**, 344 (1908); see also TREADWELL: Analytical Chemistry, Vol. II, p. 174.
- (15) HULETT: Phys. Rev. **32**, 257 (1911); **22**, 337 (1906).
- (16) LAMER AND PARKS: J. Am. Chem. Soc. **53**, 2040 (1931).
- (17) LAMER AND PARKS: J. Am. Chem. Soc. **55**, 4343 (1933).
- (18) LAMER AND PARKS: J. Am. Chem. Soc. **55**, 4350, table 7 (1933).
- (19) NONHEBEL AND HARTLEY: Phil. Mag. **50**, 729 (1925).
- (20) ONSAGER: Chem. Rev. **13**, 73 (1933).
- (21) OWEN: J. Am. Chem. Soc. **54**, 1758 (1932).
- (22) PARKS AND LAMER: J. Am. Chem. Soc. **56**, 90 (1934).
- (23) PEARCE AND HART: J. Am. Chem. Soc. **44**, 2411 (1922).
- (24) STOUT AND SCHUETTE: Ind. Eng. Chem., Anal. Ed. **5**, 100 (1933).
- (25) VOSBURGH AND EPPLEY: J. Am. Chem. Soc. **47**, 1255 (1925).
- (26) WOODMAN: Food Analysis, p. 523. McGraw-Hill Book Co., New York (1931).
- (27) ZWICKY: Physik. Z. **27**, 271 (1926).

THE SOLUBILITY OF LEAD SULFATE IN AQUEOUS SOLUTIONS OF SULFURIC ACID AT HIGH CONCENTRATIONS

H. D. CROCKFORD

Department of Chemistry, University of North Carolina, Chapel Hill, N. C.

AND

J. A. ADDLESTONE

Department of Chemistry, Virginia Polytechnic Institute, Blacksburg, Virginia

Received August 20, 1935

Crockford and Brawley (1) have determined the solubility of lead sulfate in aqueous sulfuric acid solution up to 80 per cent acid at 0°, 25°, 35°, and 50°C. Donk (2) has made a systematic study of the same system up to approximately 100 per cent acid at 0°, 50°, 100°, 150°, and 200°C. His work was concerned principally with the composition of the solid phases and his actual solubility data are quite meager, in some cases being completely lacking. A complete discussion of the relationships in the binary system sulfuric acid–water is given by Mellor (3).

The purpose of the work reported in this paper was to add to the data of the ternary system, particularly at the higher acid concentrations. To this end solubility data have been determined at acid concentrations up to approximately 104 per cent sulfuric acid, corresponding to 80.5 per cent sulfur trioxide, at 0°, 25°, 35°, and 50°C. The eutectic temperature in the binary system lead sulfate–sulfuric acid has also been determined.

EXPERIMENTAL

The usual procedure employed for solubility measurements was followed. Various mixtures were allowed to come to equilibrium in glass-stoppered bottles, properly agitated in constant temperature baths. The temperatures were constant to $\pm 0.02^\circ\text{C}$. at the three higher temperatures. For the 0°C. isotherm the temperature was never over 0.1°C. Equilibrium was rapidly attained in those cases in which lead sulfate was the only solid phase. When sulfuric acid or one of its hydrates was a solid phase, considerable trouble from supercooling was experienced.

The materials employed were prepared and purified according to the methods used by Crockford and Brawley (1). The analytical procedures were likewise the same.

The compositions of the solid phases were obtained by the method of

intersecting tie-lines. For the determination of the lead sulfate-sulfuric acid eutectic temperature, the usual cooling curve method was used.

DATA AND CONCLUSIONS

The data obtained for the 25°, 35°, and 50°C. isotherms were plotted on large coördinate paper and the best curve drawn through the points. The concentrations given in table 1 are taken from these curves. It was

TABLE 1
Solubility of lead sulfate in aqueous sulfuric acid at 25°, 35°, and 50°C.

CONCENTRATION OF ACID IN WEIGHT PER CENT	LEAD SULFATE, IN MILLIGRAMS PER 1000 G. OF SOLUTION, AT		
	25°C.	35°C.	50°C.
80	11.5	24.0	42.0
85	60.0	100.	130.
90	200	318	380
95	800	1,060	1,260
100	18,000	22,000	27,600
101	31,000	36,000	42,000
102	47,000	52,000	56,000
103	63,000	68,000	72,000

TABLE 2
Data for the 0°C. isotherm

NO.	ACID CONCENTRA- TION IN WEIGHT PER CENT	LEAD SULFATE IN MG. PER 1000 G. OF SOLUTION	SOLID PHASES
1	77.48	4.2	Lead sulfate
2	79.10	8.6	Lead sulfate and sulfuric acid monohydrate
3	89.44	42.0	Lead sulfate and sulfuric acid monohydrate
4	91.69	272	Lead sulfate
5	94.03	680	Lead sulfate
6	96.52	2200	Lead sulfate
7	97.08	3000	Lead sulfate and sulfuric acid

not thought worthwhile to give the data for the wet residues. The results agree with those of Donk, in that lead sulfate is the only solid phase at these temperatures.

In table 2 are given the data for the 0°C. isotherm as actually determined. No solutions exist above 97.08 per cent.

The lead sulfate-sulfuric acid eutectic temperature was found to be 5.4°C.

If all the data available on the ternary system are plotted it is found that

lead sulfate exists as the only solid phase over the major part of the diagram. On the lead sulfate–water side of the diagram the binary eutectic is of course at practically 0°C. On the lead sulfate–sulfuric acid side is the one eutectic whose temperature is given above. On the sulfuric acid–water side are found three hydrates of sulfuric acid. Two of these have definite melting points. Only the monohydrate exists above 0°C. Within the diagram will be four ternary eutectics, all of which will occur very close to the sides of the diagram.

The 0°C. isotherm shows the existence of five solubility curves. On two of these the solid phase is lead sulfate; on two others it is the monohydrate of sulfuric acid; on the other it is anhydrous sulfuric acid. The values of the acid concentrations at the intersections of these curves (solutions 2, 3, and 7), are essentially the same as the values given by Donk.

SUMMARY

The solubility of lead sulfate in various solutions of sulfuric acid at concentrations above 80 per cent and at 0°, 25°, 35°, and 50°C. has been determined.

The solid phase at 25°, 35°, and 50°C. is always lead sulfate. At 0°C. sulfuric acid and sulfuric acid monohydrate also exist as solids

REFERENCES

- (1) CROCKFORD AND BRAWLEY: *J. Am. Chem. Soc.* **56**, 2600 (1934).
- (2) DONK: *Chem. Weekblad* **13**, 92 (1916).
- (3) MELLOR: *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. X, p. 352. Longmans, Green and Co., London and New York (1930).

COLLOIDAL SOLUTIONS IN CONCENTRATED ELECTROLYTES¹

ANDR. VOET

Department of Chemistry, University of Amsterdam, Amsterdam, Holland

Received April 24, 1955

INTRODUCTION

If concentrated sulfuric acid be electrolyzed with a direct current of high current density and a potential difference of, for instance, 100 volts, using electrodes of noble metals, such as gold, platinum, or palladium, after some time there will suddenly be observed in the liquid a dark color, which seems to proceed from the anode. It was thought that this phenomenon might be ascribed to the formation of a colloidal solution of palladous sulfide. In order to test this assumption, experiments were carried out which soon proved its exactness. Experiments were then performed in order to find out whether other substances are colloiddally dispersed in sulfuric acid and in other concentrated electrolytes.

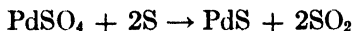
EXPERIMENTAL

1. Concentrated sulfuric acid as a dispersion medium

a. Colloidal sulfides

The palladium sulfide sol may be prepared as follows: A solution of about 200 mg. of palladous sulfate in 1 liter of commercial concentrated sulfuric acid (about 96 per cent) is heated to about 100°C., after which 100 to 200 mg. of flowers of sulfur is added. On stirring the liquid, a darkening is soon observed. After cooling, the sol is filtered through a glass filter to remove small quantities of coarser particles.

The sol formation may be represented by the following reaction:



The particle size has been determined by the usual ultramicroscopic method. If the particle is supposed cubic, the edge of the cube is found to be 97 m μ . This number is, without doubt, too high, owing to the polydispersity of the sol.

The sol may remain stable for several weeks. Finally little flakes are formed, which adhere to one another and at last sink to the bottom. This flocculate exhibits a remarkable behavior. On shaking the flakes dis-

¹ This paper is part of a thesis presented at the University of Amsterdam.

appear, and the original sol is restored completely. After a few days the flakes appear again, but can be dispersed anew by shaking. The same behavior is exhibited on centrifuging. The flakes appear on the bottom of the vessel, but disperse at once on shaking. The velocity of flocculation increases on heating, but the reversibility of the flocculate is not influenced. An "aging" phenomenon of the flocculate could not be observed; more than a year later the reversibility of the flakes was unchanged. The reversible flocculation is clearly different from a reversible sedimentation, as in the latter case the particles only sink to the bottom, while in the former case little visible flakes are formed throughout the liquid, which constantly grow and at last sink to the bottom.

On diluting the sol with water, an irreversible coagulate immediately appears.

The gold and platinum sulfide sols can be prepared in the same way and have practically the same properties. The silver sulfide sol is formed by mixing a solution of silver sulfate in the concentrated acid with a sol of sulfur in the same liquid (see below). At a temperature of about 40° to 50°C. the sol formation is observed, but at 60° to 70°C. the particles dissolve completely in the dispersion medium. When electrolyzing concentrated sulfuric acid with silver electrodes André (1) observed a brownish liquid, which he mistook for a silver sol. As a matter of fact a silver sulfide sol had been formed.

b. Colloidal metals

Colloidal metals may be prepared by reducing the dilute solutions of the salts in sulfuric acid with reducing agents such as a concentrated, freshly prepared solution of white phosphorus in ether or in carbon disulfide. The palladium sol is formed at room temperature, while sols of platinum and gold result on heating to 30° to 40°C. Reduction can also be accomplished with hydrogen at a higher temperature, but the resultant sols are less stable, owing to secondary coagulation. The palladium sol is a dark brown stable sol, which does not flocculate on heating. On dilution of the sol with water an immediate flocculation ensues. The influence of dilution on the stability of the sol is shown in table 1. Upon dilution with alcohol the sol does not coagulate, but dissolves slowly in the course of a few days.

Ultramicroscopic examination shows a fairly good monodisperse sol with slowly moving particles. The particle size has been determined for several specimens. Usually the value of the length of the edge of the supposed cubic particle is found to be between 30 and 40 $m\mu$.

Different colors are exhibited by the gold sols, from red to yellow, brownish, and blue, apparently owing to slight modifications in the manner of preparation. The most stable are the red sols, which can be prepared by reducing at the lowest possible temperature, while immediate cooling after the beginning of the reduction is necessary.

The particle size of a gold sol has been determined by the ultramicroscopic method; the length of the edge of the supposed cubic particles is found to be 44.5 $m\mu$.

The gold sols are less stable than the palladium sols and generally flocculate within a week. On heating the sols, the color changes from blue to red and yellow, and finally the sols become almost colorless. Observations of the Tyndall effect, which becomes more intense, prove that the sol flocculates.

The platinum sol is a brownish-black sol, the properties of which are practically the same as those of the gold sol.

c. Colloidal silver halides

A silver chloride sol is formed on mixing a solution of 2 or 3 milliequivalents of silver sulfate in sulfuric acid with an equivalent quantity of hydrochloric acid. It is a white opalescent liquid, which resembles a silver

TABLE 1
Influence of dilution on the stability of the sol

NO	COMPOSITION OF THE MEDIUM		CONDITION OF THE SOL
	Sulfuric acid	Water	
	cc	cc.	
1	25	0	Stable
2	20	5	Flocculation in one day
3	15	10	Flocculation in a few hours
4	10	15	Instant flocculation
5	5	20	Instant flocculation

chloride sol in water. After a few days the sol flocculates. The stability is not influenced if exactly equivalent quantities of silver sulfate and hydrochloric acid be mixed, or if one of these components be slightly in excess of the other.

The silver bromide and silver iodide sols are formed when a halide is added to an excess of a silver sulfate solution in sulfuric acid. In this case the formation of the silver halides takes place much more rapidly than the decomposition of the hydrobromic and hydrochloric acids. The colloidal silver bromide is whitish-yellow, the silver iodide yellow, in color. The halide sols in sulfuric acid flocculate on dilution with water and have practically the same properties.

d. Colloidal sulfur

The sulfur sol may be prepared by adding a drop of a concentrated solution of sodium sulfide to concentrated sulfuric acid, while stirring the liquid steadily. The sol formation is due to decomposition of the polysulfide which is always present in sodium sulfide. The slow decomposition of the

hydrogen sulfide thus formed causes a gradual increase in the sol concentration.

e. Colloidal organic substances

If an organic substance be brought into contact with concentrated sulfuric acid, it is carbonized in many cases, while the acid is colored brown to black. Ultramicroscopic examinations show that a sol has been formed.

If a drop of a dilute sucrose solution be mixed with sulfuric acid and the mixture be kept at 150°C. for some time, a dark brown sol results, which shows a number of intensely light-scattering, slowly moving particles. On dilution with water, the sol flocculates. The analysis of the flakes gave the following results: C = 64.73 per cent, H = 3.18 per cent, no ash. Sulfur was detected only qualitatively. It is evident that the dispersed phase is a sulfurated product of sucrose.

Sabbatini (4) prepared a sol in water (which he mistook for a carbon sol) by pouring the reaction product of sucrose and sulfuric acid into water and dialyzing. As a matter of fact the original solution in sulfuric acid was already a colloidal system.

f. Colloidal carbon

A carbon sol may be obtained by electrolyzing sulfuric acid with carbon electrodes, using a direct or alternating current with a potential difference of 100 volts. To remove the coarser particles the sol is filtered through a glass filter. The sol is stable for some time, but on dilution with water it flocculates immediately.

2. *Other dispersion media*

a. Phosphoric acid

Colloidal sulfides may be obtained by passing hydrogen sulfide through a dilute solution of salts of the respective metals in commercial concentrated phosphoric acid, which contains about 89 per cent of the acid, while other sols are prepared as in the sulfuric acid medium and generally show the same properties.

A different behavior is exhibited by the silver halide sols, which show nearly the same stability if the quantities of silver and halide be exactly equivalent or if a slight excess of halide be present, but which are much more stable if silver be slightly in excess.

The results of a determination of the particle size of a gold sulfide (Au_2S_3) sol gave a value of 67 $\text{m}\mu$ for the length of the edge of a supposed cubic particle.

All these sols flocculate on dilution with water and in several cases with organic liquids, as is shown in tables 2 and 3 for a gold sulfide sol.

b. Saturated salt solutions as dispersion media

Generally all saturated solutions of very soluble salts have a stabilizing action on colloids, but there are only a few salts of which the saturated solution has been found to be a medium for stable colloids, for instance, saturated solutions of the acetates of potassium and ammonium, or the chlorides of calcium and magnesium. A more extensive study has been made of the potassium acetate and calcium chloride solutions, which can be media for several stable metal, sulfide, and other sols. In most cases the sols can be stabilized by very small quantities of gelatin. On dilution, as well as on dialysis, stabilized and non-stabilized sols flocculate.

TABLE 2

Effect of dilution with water on a gold sulfide sol

NO	COMPOSITION OF THE DISPERSION MEDIUM		CONDITION OF THE SOL
	Phosphoric acid	Water	
	cc.	cc	
1	25	0	Stable
2	20	5	Flocculates slowly
3	15	10	Flocculates more quickly
4	10	15	Instant flocculation
5	5	20	Instant flocculation

TABLE 3

Effect of dilution with alcohol on a gold sulfide sol

NO.	COMPOSITION OF THE DISPERSION MEDIUM		CONDITION OF THE SOL
	Phosphoric acid	Alcohol	
	cc	cc.	
1	25	0	Stable
2	20	5	Flocculates slowly
3	15	10	Flocculates more quickly
4	10	15	Instant flocculation
5	5	20	Instant flocculation

3. Physical properties

a. Conductivity

The concentrated electrolyte solutions which have been used as dispersion media have a very high conductivity as compared with ordinary sols. The specific conductivity of sols in water or in organic media seldom exceeds a value $K = 3 \times 10^{-4}$. Table 4 shows the specific conductivity of the different media.

b. Electrokinetic potential

The usual methods for the determination of the electrokinetic potential of the particles cannot be applied, owing to the high conductivity of the medium. In a few cases it was possible to overcome this difficulty, making use of the property of sulfuric acid that mixtures of it with other substances sometimes have a low conductivity. A solution of sulfur trioxide in sulfuric acid has been made, containing about 65.1 per cent free sulfur trioxide, which has a very low conductivity. Cataphoresis has been carried out with a palladium sulfide sol in this medium in a specially modified Burton apparatus. No movement whatever of the boundary could be detected. The same phenomenon has been observed with a palladium sol in a mixture of about equal volumes of sulfuric acid and glacial acetic acid.

TABLE 4
Specific conductivity of the different media

MEDIA	$K_{18} \times 10^4$
Sulfuric acid, 96 per cent.....	940
Phosphoric acid, 87 per cent.....	710
Calcium chloride, saturated.....	950
Potassium acetate, saturated.....	520

TABLE 5
Relative viscosity of the dispersion media

MEDIA	RELATIVE VISCOSITY AT 25°C WATER = 1
Sulfuric acid, 96 per cent.....	20.4
Phosphoric acid, 89 per cent.....	55.2
Calcium chloride, solution saturated at room temperature.....	5.89
Potassium acetate, solution saturated at room temperature.....	11.91
Phosphoric acid, 44.5 per cent.....	6.15

c. Relative viscosity

The relative viscosity of these sols has been determined with a viscosimeter of the Jones-Veazy type (3) in a thermostat at 25°C. No difference in the viscosity of the sols and the dispersion media could be detected.

DISCUSSION

According to the current views, the stability of a sol is ascribed to a potential difference between the particle and the medium or to a solvation of the particle. As neither a movement in the Burton apparatus nor a high relative viscosity could be detected, both of these explanations seemed to be out of the question. It might be supposed that the particles are dis-

charged by the electrolyte, but that the very great viscosity of the dispersion medium is the cause of an extremely slow flocculation and therefore of the apparent stability of the sol. Inspection of table 5 shows at once, however, that this assumption is not correct. The maximum viscosity reaches the value 55.2, in relation to water, but the proportion between the stability of sols in concentrated phosphoric acid and in dilute aqueous solution is much higher, since the time necessary for flocculation is in the latter case measured in seconds and minutes, but in the former in days and weeks. Other observations lead to the same conclusion. A sol in phosphoric acid which has been diluted to twice its volume is flocculated within a short time, yet the table shows that the viscosity of this medium is higher than the viscosity of a saturated solution of calcium chloride, which can be a medium for a stable sol. A red gold sol can be made in a concentrated solution of sucrose, which has a high viscosity. Yet a small quantity of electrolyte turns the color from red to blue within a short time. In this case the high viscosity does not stabilize.

On the other hand it must be considered that, owing to the very small concentration of the sols, their relative viscosity will, according to Einstein's law (2), not differ from unity by an observable amount, even if a larger quantity of solvent should adhere to the particle.

Again, the phenomenon of reversible flocculation may be brought forward, which is in some respects analogous to the reversible isothermal sol-gel transformation usually called thixotropy. This phenomenon is exhibited by some colloids which have a more or less lyophilic character, such as the ferric oxide sol, the vanadium pentoxide sol, etc., and is explained by assuming a very weak bond between the particles which are surrounded by layers of adhering liquid. Now in this case the concentration of the colloid is so high that all the liquid is enclosed within the large gel complex, and the free dispersion medium has completely disappeared. However, this behavior may also be exhibited by a dilute colloid. In this case the quantity of liquid is too large to be totally enclosed, but solvated flakes are formed, the thixotropy of which is shown by a total dispersion on shaking. This phenomenon has been observed by H. Werner (5), who studied a suspension of *Bolus alba*. This clay suspension flocculated after some time, but the flakes, which were covered by a liquid layer, could be dispersed by shaking.

This picture is quite identical with the reversible flocculation exhibited by the palladium sulfide sol in sulfuric acid and by other sols mentioned in the experimental part. It is therefore assumed that the particles of these sols, which show thixotropy in dilute solution, are covered by a layer of adhering liquid medium and possess in some degree lyophilic properties.

The conception of thixotropy will have to be extended and defined as a reversible isothermal transition from a sol to a conglomerate, while, more-

over, the latter may equally well be a gel as a flocculate. This point of view can be proved by the observation that some colloids show thixotropy in concentrated solution, but reversible flocculation when diluted. This typical behavior is clearly shown by bentonite.

In accordance with this hypothesis it may be assumed that in concentrated salt solutions an adsorption of the salt will ensue. The hydration of the adsorbed salt will hydrate the particle, which therefore will be stabilized. This hypothesis is supported by the observation that, in general, the more hydrated the ions of the salt are, the higher is the stability of the colloidal systems.

The protective action of proteins is explained by a hydration which stabilizes the particle. Thus the hydrating action of the salt in concentrated solution can be partially supplied by gelatin. Now it is clear that with small concentrations of electrolytes more gelatin will be needed to stabilize the colloids if the salt concentration is increased, while in concentrated salt solutions the reverse is true. In the former case the hydrating gelatin is necessary to obtain the minimum stability, which is decreased by the action of the electrolytes; in the latter case the hydration of the adsorbed salt acts as a substitute for the hydration of the protein.

CONCLUSION

From this study it may be concluded that the influence of electrolytes on colloids is more complicated than was formerly thought. A hydrophobic sol which is perfectly free of electrolytes is generally unstable, as a small quantity of electrolyte is necessary to form the double layer. This quantity is stabilizing. A somewhat larger quantity produces flocculation. Finally a very high concentration of electrolytes has again a stabilizing influence. In general, a colloidal system, according to the electrolyte concentration, has two stable and two unstable zones.

SUMMARY

1. A colloidal solution may be stable in solutions of concentrated electrolytes.
2. Methods of preparation have been described for sols of metals, sulfides, silver halides, sulfur, carbon, etc. in dispersion media such as concentrated sulfuric acid and phosphoric acid and saturated solutions of salts, such as calcium chloride and potassium acetate.
3. Sols in solutions of concentrated electrolytes do not show any electrokinetic potential difference, nor an increase in relative viscosity.
4. Some colloids in concentrated electrolytes exhibit thixotropy.
5. The hypothesis that the stability of colloidal systems in concentrated electrolytes is caused by solvation is supported by several arguments.

The author is much indebted to Dr. E. H. Buchner, Director of this laboratory, for his interest and kind advice.

REFERENCES

- (1) ANDRÉ, H.: *Compt. rend.* **181**, 243 (1925).
- (2) EINSTEIN, A.: *Ann. Physik* [4] **19**, 289 (1905).
- (3) JONES AND VEAZY: *Z. physik. Chem.* **61**, 64 (1905).
- (4) SABBATINI: *Kolloid-Z.* **15**, 23 (1914).
- (5) WERNER, H.: *Ber.* **62**, 1525 (1929).

THE SOLUBILITY OF LEAD BROMATE AND ITS ACTIVITY COEFFICIENTS IN SOLUTIONS OF ELECTROLYTES

F. H. MacDOUGALL AND EVERETT J. HOFFMAN¹

School of Chemistry, University of Minnesota, Minneapolis, Minnesota

Received September 26, 1935

INTRODUCTION

This investigation was undertaken in order to study the effect of nitrates of certain uni- and bi-valent metals on the solubility and activity coefficients of a bi-univalent salt, and to compare observed results with those computed on the basis of modern theories of electrolyte solutions. For this purpose the solubility of lead bromate was determined at 25°C. in aqueous solutions of various concentrations of the nitrates of sodium, potassium, lithium, calcium, strontium, and lead.

W. Böttger (1) determined the solubility of lead bromate in water and found it to be 13.37 g. (0.0289 mole) per liter of solution at 19.96°C. From conductance data he calculates that the saturated solution is 72 per cent ionized. We find the solubility of lead bromate in water at 25°C. to be 0.03437 mole per liter. The density of this saturated solution is 1.0112.

MATERIALS AND PROCEDURE

Water. The solutions were prepared with "conductivity" water which was obtained by the distillation of distilled water over sodium hydroxide and potassium permanganate in a tin-lined vessel.

Lead bromate. The lead bromate was prepared by the following method: A solution of sodium bromate heated to 30°C. was added to a solution of lead nitrate at the same temperature with constant stirring. The lead bromate was allowed to settle, and the solution was cooled. The supernatant liquid was then decanted, and the lead bromate was washed several times by decantation, filtered, and washed again on the filter. The lead bromate was then washed thoroughly with pure 95 per cent alcohol and absolute ether and dried in a vacuum desiccator over magnesium perchlorate at room temperature. Attempts to dry the lead bromate by heating resulted in decomposition as described by Rammelsberg (5).

¹ This paper gives the essential portions of the thesis presented by E. J. Hoffman in June, 1935, to the Graduate Faculty of the University of Minnesota in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

Nitrates. The nitrates were of the best quality available. They were crystallized once and sometimes twice from conductivity water. They were then dehydrated thoroughly.

Sodium thiosulfate solution. The sodium thiosulfate solution used for analysis was prepared by the method of Watson (6).

Preparation of solutions. Conductivity water was added by means of an accurately calibrated pipet (100-cc. capacity) to glass-stoppered bottles containing previously weighed quantities of the nitrate and an excess of lead bromate. All weighings were corrected for buoyancy. A heavy coat of paraffin was applied to the stoppers of the bottles after the solutions were prepared, and the bottles were then mechanically rotated in a water-bath at $25.00 \pm 0.05^\circ\text{C}$. for several hours until equilibrium was established.

Method of analysis. After equilibrium had been established, the bottles were removed from the rotator and, still immersed almost completely, were held stationary in the water-bath to allow the excess lead bromate to settle. The clear solution was then drawn off by means of vacuum into an Erlenmeyer flask almost completely immersed in the water-bath (4). A small plug of absorbent cotton was placed in the end of the delivery tube to prevent the passage of any solid particles of lead bromate during the transfer of the solution from the bottle to the flask. Four 10-cc. samples of the solution were withdrawn from the flask by means of an accurately calibrated pipet and transferred to previously weighed weighing bottles. These samples were then accurately weighed in order to determine the densities of the solutions. These solutions were then washed into 500-cc. glass-stoppered Erlenmeyer flasks containing a solution of potassium iodide acidified with hydrochloric acid, and were titrated with 0.3 *M* sodium thiosulfate prepared by the method described above. A 0.2 per cent starch solution, containing 0.1 per cent salicylic acid as preservative, was used as indicator. Analysis of each concentration of nitrate solution was thus run in quadruplicate. It was possible from a knowledge of the weight of each constituent of the solution and the density to determine the concentrations as molality, molarity, or mole fraction.

EXPERIMENTAL RESULTS

Tables 1 to 6 list the solubilities at 25°C . of lead bromate in aqueous solutions of the nitrates at various concentrations. We denote in general the molality and molarity of a solute in a solution by *m* and *c*, respectively. The normalized mole-fraction, \bar{x} , of Pb^{++} is calculated on the assumption of complete ionization of the dissolved salts. Normalized mole-fraction (4) is equal to the mole-fraction multiplied by the factor 55.51. The ionic strength, *S*, given in these tables is calculated on the basis of complete

TABLE 1

Solubility, equilibrium constants (K_1 and K_2), and activity coefficients of lead bromate in the presence of potassium nitrate at 25°C.

c KNO ₃	d SATU- RATED SOLUTION	c Pb(BrO ₃) ₂	\bar{z} Pb(BrO ₃) ₂	A	α	K_1	f_1^2	f^a	γ^a
0.	1.0112	0.03437	0.03447		0.4660	0.01980	0.574	0.365	0.364
0.04883	1.0156	0.03924	0.03938	0.6348	0.5222	0.01975	0.471	0.320	0.318
0.09934	1.0181	0.04378	0.04405	0.5720	0.5610	0.01987	0.406	0.286	0.284
0.1956	1.0286	0.05104	0.05129	0.5650	0.6162	0.01985	0.330	0.245	0.243
0.2950	1.0378	0.05798	0.05828	0.5400	0.6569	0.01987	0.280	0.216	0.213
0.3901	1.0456	0.06396	0.06434	0.5313	0.6878	0.01983	0.246	0.196	0.192
0.4857	1.0547	0.07003	0.07042	0.4481	0.7129	0.01983	0.220	0.179	0.175
0.5784	1.0608	0.07577	0.07636	0.4522	0.7330	0.01986	0.200	0.165	0.161
0.7671	1.0776	0.08734	0.08805	0.5886	0.7662	0.01987	0.169	0.143	0.138
0.9339	1.0906	0.09818	0.09921	0.4587					
1.1850	1.1127	0.1134	0.1146	0.4181	Av. = 0.01984				
1.4419	1.1327	0.1293	0.1293	0.4363	$A = 0.30; K_2 = 0.01452; \bar{x}_0 = 0.02441; \alpha_0 = 0.3120$				
1.8314	1.1664	0.1550	0.1576	0.4058					
2.0352	1.1833	0.1685	0.1717	0.3845					
2.2469	1.2011	0.1782	0.1815	0.3973					
2.4449	1.2161	0.1799	0.1830	0.4164					
2.6423	1.2220	0.1732	0.1769						

TABLE 2

Solubility, equilibrium constants (K_1 and K_2), and activity coefficients of lead bromate in the presence of sodium nitrate at 25°C.

c NaNO ₃	d SATU- RATED SOLUTION	c Pb(BrO ₃) ₂	\bar{z} Pb(BrO ₃) ₂	A	α	K_1	f_1^2	f^a	γ^a
0.	1.0112	0.03437	0.03447		0.4610	0.01992	0.581	0.365	0.364
0.04833	1.0141	0.03884	0.03900	0.7294	0.5137	0.01988	0.483	0.323	0.321
0.1013	1.0184	0.04317	0.04335	0.6789	0.5523	0.01995	0.418	0.290	0.289
0.1991	1.0266	0.04984	0.04997	0.6483	0.6036	0.01997	0.345	0.252	0.249
0.2963	1.0334	0.05580	0.05602	0.6329	0.6397	0.02003	0.299	0.225	0.222
0.3938	1.0424	0.06144	0.06157	0.6143	0.6683	0.02006	0.265	0.204	0.201
0.4892	1.0465	0.06430	0.06454	0.6585	0.6959	0.01959	0.241	0.195	0.191
0.5874	1.0564	0.07112	0.07122	0.6003	0.7121	0.01998	0.220	0.177	0.172
0.7776	1.0697	0.08024	0.08033	0.4830	0.7430	0.01997	0.189	0.157	0.152
0.9655	1.0837	0.08899	0.08899	0.5709	0.7667	0.01996	0.168	0.141	0.136
1.1970	1.1000	0.09967	0.09962	0.5535					
1.4241	1.1158	0.1098	0.1097	0.5406	Av. = 0.01993				
1.8655	1.1460	0.1295	0.1292	0.5050	$A = 0.385; K_2 = 0.01453; \bar{x}_0 = 0.02456; \alpha_0 = 0.3110$				
2.2921	1.1754	0.1487	0.1484	0.5009					
2.6860	1.2010	0.1651	0.1648	0.4911					
3.4672	1.2530	0.1990	0.1986	0.4725					
4.8546	1.3378	0.2536	0.2546	0.4546					
6.0912	1.4172	0.3026	0.3041	0.4420					
7.1770	1.4824	0.3416	0.3446	0.5327					

TABLE 3

Solubility, equilibrium constants (K_1 and K_2), and activity coefficients of lead bromate in the presence of lithium nitrate at 25°C.

LiNO_3	d SATURATED SOLUTION	$\text{Pb}(\text{BrO}_4)_2$	$\text{Pb}(\text{BrO}_3)_2$	A	α	K_1	f_1^*	f^*	γ^*
0.	1.0112	0.03437	0.03447		0.4542	0.02007	0.590	0.365	0.364
0.04925	1.0135	0.03849	0.03864	0.8663	0.5043	0.02001	0.496	0.326	0.325
0.09873	1.0158	0.04224	0.04244	0.7837	0.5369	0.02014	0.438	0.297	0.295
0.2049	1.0244	0.04874	0.04886	0.7643	0.5870	0.02021	0.363	0.258	0.255
0.3012	1.0293	0.05365	0.05379	0.7500	0.6192	0.02025	0.320	0.234	0.231
0.3933	1.0348	0.05800	0.05812	0.7366	0.6434	0.02029	0.290	0.217	0.213
0.4929	1.0399	0.06206	0.06217	0.7333	0.6655	0.02026	0.266	0.202	0.198
0.5815	1.0446	0.06517	0.06525	0.7373	0.6828	0.02015	0.248	0.193	0.188
0.7751	1.0549	0.07225	0.07226	0.7226	0.7117	0.02014	0.218	0.174	0.169
0.9644	1.0649	0.07867	0.07849	0.7102	Av. = 0.02017				
1.4259	1.0880	0.09337	0.09310	0.6814					
1.8680	1.1084	0.1061	0.1057	0.6623	$A = 0.50; K_2 = 0.01453; \bar{x}_0 = 0.02498; \alpha_0 = 0.3079$				
2.3032	1.1302	0.1190	0.1184	0.6412					
2.7213	1.1507	0.1310	0.1300	0.6257					
3.5192	1.1887	0.1534	0.1518	0.5919					
4.9703	1.2562	0.1930	0.1904	0.5685					

TABLE 4

Solubility of lead bromate in the presence of strontium nitrate at 25°C. Values of α and A calculated for saturated solutions of lead bromate in the presence of strontium nitrate

$\text{Sr}(\text{NO}_3)_2$	d SATURATED SOLUTION	$\text{Pb}(\text{BrO}_4)_2$	$\text{Pb}(\text{BrO}_3)_2$	A	α	A^*
0.	1.0112	0.03437	0.03447			
0.005566	1.0117	0.03581	0.03595	0.8342	0.476	0.478
0.01031	1.0129	0.03702	0.03717	0.8929	0.490	0.485
0.01958	1.0144	0.03893	0.03911	0.9257	0.511	0.518
0.05020	1.0226	0.04455	0.04471	0.8892	0.563	0.530
0.09944	1.0332	0.05180	0.05199	0.8441	0.617	0.529
0.1975	1.0548	0.06339	0.06354	0.7972	0.680	0.530
0.2949	1.0741	0.07301	0.07318	0.7676	0.719	0.529
0.3903	1.0933	0.08177	0.08191	0.7427	0.749	0.525
0.4856	1.1107	0.08939	0.08961	0.7281	0.768	0.525
0.5804	1.1301	0.09739	0.09750	0.7092	0.785	0.520
0.7614	1.1627	0.1110	0.1113	0.6842	0.811	0.514
0.9446	1.1971	0.1249	0.1253	0.6608	0.831	0.505
1.3742	1.2748	0.1535	0.1542	0.6297	0.862	0.495
1.7789	1.3438	0.1765	0.1781	0.6127	0.880	0.480
2.1599	1.4084	0.1955	0.1979	0.6031		
2.5197	1.4668	0.2105	0.2140	0.5980		
2.8704	1.5261	0.2228	0.2267	0.5976		

* Calculated from equations 24 and 25.

TABLE 5

Solubility of lead bromate in the presence of calcium nitrate at 25°C. Values of α and A calculated for saturated solutions of lead bromate in the presence of calcium nitrate

$\text{Ca}(\text{NO}_3)_2$	d SATURATED SOLUTION	$\text{Pb}(\text{BrO}_3)_2$	\bar{x} $\text{Pb}(\text{BrO}_3)_2$	A	α	A^*
0.	1.0112	0.03437	0.03447			
0.006271	1.0099	0.03565	0.03584	1.2263	0.475	0.541
0.01116	1.0117	0.03640	0.03656	1.4195	0.483	0.636
0.02156	1.0135	0.03921	0.03941	0.9559	0.514	0.533
0.05162	1.0195	0.04298	0.04314	1.1370	0.549	0.676
0.1215	1.0313	0.05387	0.05409	0.8693	0.630	0.556
0.1975	1.0425	0.06202	0.06231	0.8353	0.674	0.558
0.3352	1.0643	0.07497	0.07522	0.7874	0.726	0.551
0.4920	1.0869	0.08769	0.08808	0.7513	0.764	0.544
0.5764	1.0997	0.09473	0.09496	0.7318	0.780	0.537
0.7780	1.1283	0.1105	0.1108	0.6945	0.810	0.522
0.9524	1.1457	0.1194	0.1204	0.6908	0.825	0.528
1.3805	1.2090	0.1435	0.1437	0.6753	0.852	0.527
1.7872	1.2607	0.1647	0.1653	0.6502		
2.1719	1.3074	0.1813	0.1823	0.6408		
2.5361	1.3489	0.1944	0.1963	0.6354		
3.1950	1.4215	0.2118	0.2154	0.6347		

* Calculated from equations 24 and 25.

TABLE 6

Solubility of lead bromate in the presence of lead nitrate at 25°C.

$\text{Pb}(\text{NO}_3)_2$	d SATURATED SOLUTION	$\text{Pb}(\text{BrO}_3)_2$	$\sqrt[3]{\frac{L_c}{4}}$	\bar{x} $\text{Pb}(\text{BrO}_3)_2$	$\sqrt[3]{\frac{L_x}{4}}$	A
0.	1.0112	0.03437	0.03437	0.03447	0.03447	
0.004947	1.0104	0.03371	0.03529	0.03388	0.03546	0.8167
0.009921	1.0118	0.03332	0.03635	0.03348	0.03651	0.7564
0.01990	1.0132	0.03258	0.03819	0.03277	0.03841	0.7697
0.04981	1.0219	0.03161	0.04333	0.03176	0.04354	0.7707
0.09940	1.0356	0.03145	0.05058	0.03160	0.05083	0.7533
0.1978	1.0643	0.03264	0.06262	0.03318	0.06366	0.6973
0.2955	1.0936	0.03457	0.07333	0.03465	0.07352	0.6942
0.3882	1.1120	0.03657	0.08283	0.03697	0.08372	0.6603
0.4871	1.1480	0.03876	0.09245	0.03887	0.09272	0.6501
0.5804	1.1735	0.04102	0.1015	0.04119	0.1017	0.6330
0.7672	1.2290	0.04572	0.11193	0.04583	0.1196	0.6027
0.9470	1.2786	0.05046	0.1364	0.05069	0.1371	0.5770
1.1663	1.3402	0.05613	0.1568	0.05648	0.1577	0.5544
1.3807	1.4011	0.06183	0.1767	0.06226	0.1779	0.5397

ionization of the dissolved salts. The ionic strength is defined by the equation

$$S = \frac{1}{2} \sum c_i z_i^2 \quad (1)$$

where c_i is the molar concentration and z_i is the valence of an ion of the i^{th} kind.

It will be observed that in general the solubility of lead bromate increases with increasing concentration of added nitrate. In the presence, however, of lead nitrate, the solubility of the bromate diminishes to a minimum and then increases. The data obtained with lead nitrate as added salt can be best compared with those found with other salts by means of the quantity $\sqrt[3]{\frac{L_c}{4}}$, where L_c is the ionic product of lead bromate, i.e.,

$$L_c = [\text{Pb}^{++}] [\text{BrO}_3^-]^2 \quad (2)$$

calculated on the assumption of complete ionization. When the added salt has no ion in common with lead bromate, it is readily seen that

$$\sqrt[3]{\frac{L_c}{4}} = [\text{Pb}^{++}] = c = [\text{Pb}(\text{BrO}_3)_2] \quad (3)$$

When the added salt is lead nitrate of concentration c_a ,

$$\sqrt[3]{\frac{L_c}{4}} = \sqrt[3]{(c + c_a)c^2} \quad (4)$$

We have accordingly included in table 6 the values of $\sqrt[3]{\frac{L_c}{4}}$ which are seen to increase in the normal way with increasing ionic strength of the solution.

The solubility data are represented graphically in figure 1. It will be seen that, at a given ionic strength, the increase in the solubility (or solubility product, L_c) due to added nitrate diminishes in the order, potassium nitrate, sodium nitrate, lead nitrate, lithium nitrate, strontium nitrate, calcium nitrate.

The solubility data obtained were used to test the applicability of the Debye-Hückel (2) equation, which becomes for a bi-univalent salt in aqueous solution at 25°C.,

$$\begin{aligned} -\log f &= \log \bar{x} - \log \bar{x}_0 = \frac{1.009S^{\frac{1}{2}}}{1 + AS^{\frac{1}{2}}} \\ &= \frac{1.009S^{\frac{1}{2}}}{1 + 0.3283 \times 10^6 a S^{\frac{1}{2}}} \end{aligned} \quad (5)$$

In this equation \bar{x}_0 is the normalized activity and \bar{x} is the normalized mole-fraction of lead ion (or of bromate ion) for an ionic strength S , and a is the

mean ionic diameter parameter. It is seen that \bar{x}_0 may be looked on as the value of \bar{x} (the normalized mole-fraction of Pb^{++} in a saturated solution of lead bromate) extrapolated to a value of $S = 0$. This extrapolated value of \bar{x} is equal to m_0 and approximately equal to c_0 , the extrapolated values

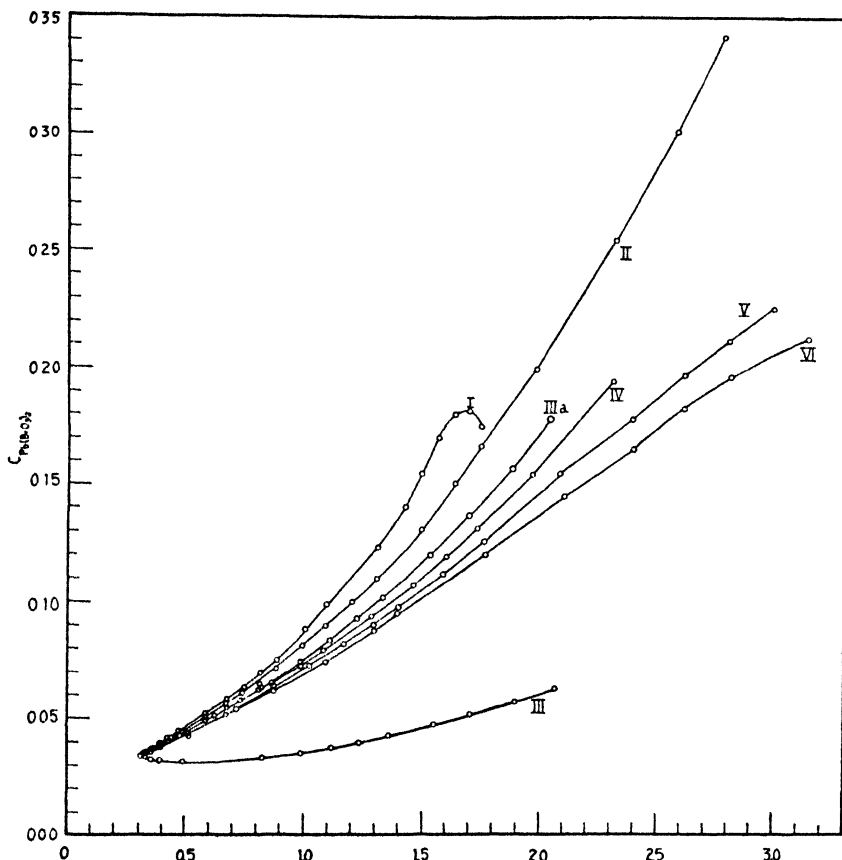


FIG. 1. Solubility of lead bromate in the presence of electrolytes. I, KNO_3 ; II, NaNO_3 ; III, $\text{Pb}(\text{NO}_3)_2$; IIIa, values of $\frac{\sqrt{L_e}}{4}$ for lead nitrate solutions; IV, LiNO_3 ; V, $\text{Sr}(\text{NO}_3)_2$; VI, $\text{Ca}(\text{NO}_3)_2$.

of the molality and molarity, respectively, of a saturated solution of lead bromate.

The two unknowns, \bar{x}_0 and A (or a), can be calculated by means of equation 5 from two sets of corresponding values of x and S . In each case the values of \bar{x} and S for lead bromate in pure water were combined successively with the corresponding values of these quantities for solutions containing increasing concentrations of added nitrate. If, for a given added electro-

lyte, a fairly constant series of values of A (or of x_0) is obtained, especially for the more dilute solutions, we may conclude that the postulates of the Debye theory are satisfied. These include the assumption that the electrolytes dealt with are virtually completely ionized.

In column 5 of tables 1 to 5 and in column 7 of table 6 are given the values of A and \bar{x}_0 calculated in the manner described for each series of solutions. It will be observed that in each case the values of A are far from being constant. There is a marked decrease in A with increasing ionic strength. We can conclude, therefore, that, if we postulate that lead bromate and the added salts are completely ionized, equation 5 is *not* applicable to aqueous solutions of lead bromate in the presence or absence of other electrolytes. We shall examine later the consequences that follow from the assumption that, in saturated solutions, lead bromate is only partially ionized.

THE HÜCKEL EQUATION

In an extension of the Debye and Hückel treatment, E. Hückel (3) took into account a possible variation of the dielectric constant of a solution with the concentration of the dissolved substances. The equation he derived, as applied to the present problem, may be written,

$$\log \bar{x} = \log \bar{x}_0 + \frac{1.009S^{\frac{1}{2}}}{1 + AS^{\frac{1}{2}}} + CS \quad (6)$$

where C is a constant. For our purpose we may consider equation 6 to be an interpolation formula. The constants of the equation, \bar{x}_0 , A , and C , can be found by the solution of three simultaneous equations of the form 6, using the corresponding values of \bar{x} and S . The usefulness of equation 6 can then be tested by calculating values of \bar{x} for various values of S and comparing the calculated with the observed values. We shall omit the details of these calculations, which showed that equation 6 can reproduce with a fair degree of accuracy our experimental results. We give in table 7 the appropriate values of the constants of the Hückel equation.

INCOMPLETE IONIZATION OF TERNARY ELECTROLYTES

Since the Debye-Hückel equation has been found to be applicable to aqueous solutions of numerous simple electrolytes up to an ionic strength of at least unity, the question arises whether the failure in the present case is apparent rather than real. Now the Debye-Hückel equation has been applied to the solubility data of lead bromate on the assumption that all the salts concerned are completely ionized. This assumption was made in calculating the ionic strength S and the concentration of Pb^{++} or of BrO_3^- in any solution.

Referring to the data given in any of the tables from 1 to 6, we see that the calculated value of A decreases with increasing concentration of added

nitrate. This result may be expressed in the statement that the solubility of lead bromate *increases* more rapidly with increasing concentration of added electrolyte than would be predicted by the Debye-Hückel equation, using a value of A obtained from solutions of low ionic strength. In other words, the effective activity coefficient of lead bromate *decreases* more rapidly with increasing concentration of added salt than the theory predicts. The assumption that the *added* nitrate is only partially ionized will not, by itself, account for this behavior; in fact, if the added nitrate in the more concentrated solutions is ionized to a smaller degree than we have supposed, the solubility of lead bromate should increase less, instead of more, rapidly with increasing concentration of the added salt.

Let us suppose, however, that lead bromate in solution is either incompletely ionized or that it exists in the form of the ions PbBrO_3^+ , Pb^{++} , and BrO_3^- . It will be recalled that, in calculating A of equation 5, two solutions are compared, one containing only lead bromate and water, the

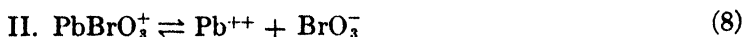
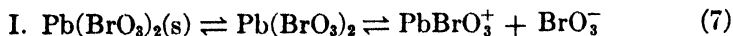
TABLE 7

Values of the Huckel constants for lead bromate in aqueous solutions of various nitrates

SOLUTION	A	$\bar{\epsilon}_0$	C
$\text{Pb}(\text{BrO}_3)_2\text{-KNO}_3$	0 8158	0 01860	0 1116
$\text{Pb}(\text{BrO}_3)_2\text{-NaNO}_3$	0 8143	0 01876	0 07132
$\text{Pb}(\text{BrO}_3)_2\text{-LiNO}_3$	0 8638	0 01904	0 04084
$\text{Pb}(\text{BrO}_3)_2\text{-Sr}(\text{NO}_3)_2$	1 0564	0 01948	0 05906
$\text{Pb}(\text{BrO}_3)_2\text{-Ca}(\text{NO}_3)_2$	1 1041	0 01961	0 05624
$\text{Pb}(\text{BrO}_3)_2\text{-Ph}(\text{NO}_3)_2$	0 9215	0 01910	0 06225

second containing in addition some soluble nitrate. If we assume that the dissolved lead bromate is not entirely in the form of Pb^{++} and BrO_3^- ions, the ionic strengths of the two solutions referred to will, of course, be less than the values calculated on the basis of complete ionization, but it is readily seen that the *decrease* in the calculated ionic strength due to our new assumption of incomplete ionization of lead bromate will be relatively greater for the first than for the second solution. Hence it follows that as we go from a solution of lead bromate only to solutions containing in addition a soluble nitrate, the activity coefficient of any ion present will decrease more rapidly than if we assume complete ionization. This is qualitatively in agreement with the observed behavior. To simplify to some extent the treatment of the problem, we make the following assumptions:

- (a) Lead bromate in aqueous solution ionizes in two stages, as given by the scheme,



- (b) The ionization according to the first stage is analogous to the ionization of a uni-univalent salt. We assume therefore that the ionization of lead bromate into PbBrO_3^+ and BrO_3^- is virtually complete.
- (c) We restrict our calculations at the present time to the case that the added nitrate is a uni-univalent salt (e.g., potassium nitrate) which we assume to be completely ionized.
- (d) In solutions containing added nitrate, it is probable that a certain amount of the intermediate ion, PbNO_3^+ , will be formed. In this preliminary treatment we assume that the amount of PbNO_3^+ formed can be neglected.
- (e) We assume that the Debye-Hückel equation is applicable to our solutions when the correct value of the ionic strength is used. It follows from this equation that in a given solution all ions having numerically equal charges have approximately equal activity coefficients and that the activity coefficient of a divalent ion is approximately equal to the fourth power of that of a univalent ion. We shall suppose that these relations are exact.

MATHEMATICAL TREATMENT

If c and c_s are the analytically determined molarities of lead bromate and of added uni-univalent salt (e.g., potassium nitrate) and if α is the degree of dissociation of the intermediate ion, PbBrO_3^+ , according to equation 8, we find

$$\begin{aligned} [\text{Pb}^{++}] &= c\alpha \\ [\text{PbBrO}_3^+] &= c(1 - \alpha) \\ [\text{BrO}_3^-] &= c(1 + \alpha) \\ [\text{K}^+] &= [\text{NO}_3^-] = c_s \end{aligned} \tag{9}$$

The ionic strength, S , of the solution is given by the equation

$$S = c(1 + 2\alpha) + c_s \tag{10}$$

Equations analogous to equation 9 may be written in terms of molalities instead of molarities.

The *actual*, normalized mole-fraction of Pb^{++} , $\bar{x}_{\text{Pb}^{++}}$, is given by the equation

$$\bar{x}_{\text{Pb}^{++}} = \frac{55.51m\alpha}{55.51 + (2 + \alpha)m + 2m_s}$$

Within at least one part in 3000, this expression may be replaced by

$$\bar{x}_{\text{Pb}^{++}} = \frac{55.51m\alpha}{55.51 + 3m + 2m_s} \tag{11}$$

on substituting 3 for the term $(2 + \alpha)$ in the denominator of the previous equation. Defining \bar{x} (without subscript) by the equation

$$\bar{x} = \frac{55.51m}{55.51 + 3m + 2m_s} \quad (12)$$

we may write

$$\bar{x}_{\text{Pb}^{++}} = \bar{x}\alpha$$

$$\bar{x}_{\text{PbBrO}_3^+} = \bar{x}(1 - \alpha) \quad (13)$$

$$\bar{x}_{\text{BrO}_3^-} = \bar{x}(1 + \alpha)$$

The quantity \bar{x} defined by equation 12 might be called the analytical (normalized) mole-fraction of lead bromate (or of lead ion).

In connection with the equilibria given in equations 7 and 8, we define the constant K_1 by the equation

$$K_1^{\frac{1}{2}} = a_{\text{Pb}^{++}} a_{\text{BrO}_3^-}^2 = f_2 f_1^2 (\bar{x})^3 \alpha (1 + \alpha)^2 \quad (14)$$

where f_1 and f_2 are activity coefficients of univalent and divalent ions respectively. Since we assume $f_2 = f_1^4$, equation 14 becomes

$$K_1 = f_1^2 \bar{x} [\alpha(1 + \alpha)^2]^{\frac{1}{2}} \quad (15)$$

Similarly we define K_2 by the equation

$$K_2 = \frac{a_{\text{Pb}^{++}} a_{\text{BrO}_3^-}}{a_{\text{PbBrO}_3^+}} = \frac{f_2 f_1}{f_1} \bar{x} \frac{\alpha(1 + \alpha)}{1 - \alpha}$$

or

$$K_2 = f_2 \bar{x} \frac{\alpha(1 + \alpha)}{1 - \alpha} = f_1^4 \bar{x} \frac{\alpha(1 + \alpha)}{1 - \alpha} \quad (16)$$

Since we have at 25°C., according to Debye and Hückel,

$$\log f_1 = -\frac{0.5045S^{\frac{1}{2}}}{1 + AS^{\frac{1}{2}}} \quad (17)$$

equations 15 and 16 may be written (bearing equation 10 in mind),

$$\log K_1 = \log \bar{x} + \frac{1}{2} \log [\alpha(1 + \alpha)^2] - \frac{1.009 \sqrt{c(1 + 2\alpha) + c_s}}{1 + A \sqrt{c(1 + 2\alpha) + c_s}} \quad (18)$$

$$\log K_2 = \log \bar{x} + \log \frac{\alpha(1 + \alpha)}{1 - \alpha} - \frac{2.018 \sqrt{c(1 + 2\alpha) + c_s}}{1 + A \sqrt{c(1 + 2\alpha) + c_s}} \quad (19)$$

Of the four unknowns in equations 18 and 19, K_1 and K_2 are constants for all solutions saturated with lead bromate, A is presumed to be a constant for a series of solutions containing a given added nitrate, and α varies from one solution to another even in a given series.

STOICHIOMETRIC ACTIVITY COEFFICIENT OF LEAD BROMATE

It is readily seen from equation 14 that the mean activity, a_{\pm} , of lead bromate in a saturated solution of this salt is equal to K_1 . It follows that the *stoichiometric* activity coefficient, f^s , of lead bromate in a saturated solution is given by the expression

$$f^s = \frac{a_{\pm}}{4^{\frac{1}{2}}x} = \frac{K_1}{4^{\frac{1}{2}}x} \quad (20)$$

Similarly it can be shown that the stoichiometric activity coefficient, γ^s , referred to molalities is given by the equation

$$\gamma^s = \frac{a_{\pm}}{4^{\frac{1}{2}}m} = \frac{K_1}{4^{\frac{1}{2}}m} \quad (21)$$

On comparison of equations 14, 15, and 20, we find

$$f^s = (f_2 f_1^2)^{\frac{1}{3}} \left[\frac{\alpha(1 + \alpha)^2}{4} \right]^{\frac{1}{3}} = f_1^2 \left[\frac{\alpha(1 + \alpha)^2}{4} \right]^{\frac{1}{3}} \quad (22)$$

Only if α were equal to unity would f^s be equal to $(f_2 f_1^2)^{\frac{1}{3}}$ or f_1^2 .

SOLUTION OF EQUATIONS 18 AND 19

Equations 18 and 19 were solved by a laborious and time-consuming method of trial which we shall illustrate in the case of the solutions containing potassium nitrate (see table 1). Two of these, that containing 0.09934 *N* potassium nitrate (solution 1) and that containing 0.7671 *N* potassium nitrate (solution 2), were selected for study. Let α_1 and α_2 represent the values of α for solutions 1 and 2 respectively. First of all, some arbitrary value for A was selected. Then a value of α_1 was assumed for solution 1. Application of equations 18 and 19 to solution 1, using these values of A and α_1 , led to a value of K_1 and a value of K_2 . This value of K_1 was then used for solution 2 and by means of equation 18 a value of α_2 was derived. This value of α_2 substituted in equation 19 gave a value of K_2 for solution 2. If this value of K_2 did not agree with the value of K_2 found from solution 1, a new value of α_1 was selected and the calculations were repeated until finally identical values of K_2 were found for both solutions.

Using this value of K_2 , equation 19 was then applied to all the other solutions of the potassium nitrate series and a value of α was calculated for each solution. Application of equation 18, using the value of α so found, gave a value of K_1 for each solution of the series. If the values of K_1 found for the various solutions did not agree with those found for solutions 1 and 2, a new value of the parameter A was selected and the whole process was repeated until finally practically identical values of K_1 were calculated for all solutions of the series up to an ionic strength of about unity.

In this way we found for saturated solutions of lead bromate in the presence of potassium nitrate, a value of A equal to 0.30, a value of K_2 equal to 0.01452, and the remarkably consistent values of K_1 (average = 0.01984) given in the seventh column of table 1. Similarly for sodium nitrate solutions, we found $A = 0.385$, $K_2 = 0.01453$, and an average value of K_1 equal to 0.01993 (see table 2). For lithium nitrate solutions, we obtained $A = 0.50$, $K_2 = 0.01453$, and K_1 (average) = 0.02017 (see table 3). The excellent agreement among the three independent determinations of both K_1 and K_2 seems to offer considerable support to the views presented by the authors.

The tables also contain values of α , the degree of ionization of PbBrO_3^+ , as well as values of f_1^2 , the latter calculated by means of the equation

$$\log f_1^2 = \log (f_2 f_1^2)^{\frac{1}{2}} = -\frac{1.009 \sqrt{c(1+2\alpha) + c_s}}{1 + A \sqrt{c(1+2\alpha) + c_s}} \quad (23)$$

The average value of K_1 from the three series is 0.01998. Tables 1, 2, and 3 contain values of the stoichiometric activity coefficients, f^* and γ^* , calculated by means of equations 20 and 21 using $K_1 = 0.01998$. These equations can also be used to calculate the stoichiometric activity coefficients for any of the solutions in tables 1 to 5. For the solutions listed in table 6, in which the added salt is lead nitrate, the stoichiometric activity coefficient, f^* , is given by the relation:

$$f^* = \frac{K_1}{L_x^{\frac{1}{2}}} \quad \text{or} \quad \frac{K_1}{4^{\frac{1}{2}} \sqrt[3]{\frac{L_x}{4}}}$$

Similarly the value of γ^* follows from the equation

$$\gamma^* = \frac{K_1}{L_m^{\frac{1}{2}}}$$

IDEAL SATURATED SOLUTION OF LEAD BROMATE

Consider the hypothetical case of a saturated aqueous solution of lead bromate in which the ionic charges no longer make the ions non-ideal solutes; in other words, let us suppose that by some means or other the various molecular species present have unit activity-coefficients. In this ideal solution, let \bar{x}_0 be the normalized mole-fraction of the lead bromate and let α_0 be the degree of ionization of the ion PbBrO_3^+ . It follows from equations 18 and 19 that

$$\log K_1 = \log \bar{x}_0 + \frac{1}{2} \log [\alpha_0(1 + \alpha_0)^2]$$

$$\log K_2 = \log \bar{x}_0 + \log \left[\frac{\alpha_0(1 + \alpha_0)}{1 - \alpha_0} \right]$$

From the accepted values of K_1 and K_2 , viz. 0.01998 and 0.01453, respectively, we readily calculate

$$\begin{aligned}\bar{x}_0 &= 0.02465 \\ \alpha_0 &= 0.3103\end{aligned}$$

Values of \bar{x}_0 and α_0 , derived from the values of K_1 and K_2 for each of the three series of solutions, are given in tables 1, 2, and 3.

APPLICATION TO CALCIUM NITRATE AND STRONTIUM NITRATE SOLUTIONS

When the added salt is of the calcium nitrate type, we obtain, instead of equations 18 and 19, the expressions

$$\log K_1 = \log \bar{x} + \frac{1}{3} \log \alpha(1 + \alpha)^2 - \frac{1.009 \sqrt{c(1 + 2\alpha) + 3c_s}}{1 + A \sqrt{c(1 + 2\alpha) + 3c_s}} \quad (24)$$

$$\log K_2 = \log \bar{x} + \log \frac{\alpha(1 + \alpha)}{1 - \alpha} - \frac{2.018 \sqrt{c(1 + 2\alpha) + 3c_s}}{1 + A \sqrt{c(1 + 2\alpha) + 3c_s}} \quad (25)$$

if we assume the added salt to be completely ionized. From equations 24 and 25 we obtain

$$2 \log K_1 - \log K_2 - \log \bar{x} = \frac{1}{3} \log \left[\frac{(1 + \alpha)(1 - \alpha)^3}{\alpha} \right] \quad (26)$$

Using the average values of K_1 and K_2 , viz. 0.01998 and 0.01453, obtained previously, we can apply equation 26 to each of the series of solutions (see tables 4 and 5), and calculate for each solution the value of α . Substituting this value of α in equation 24, we can determine the magnitude of the parameter A . The results obtained by these calculations appear in columns 6 and 7 of tables 4 and 5. We include here only solutions which contained an added nitrate.

The values of A so calculated exhibit a remarkable degree of constancy if we except solutions 3 and 5 in the calcium nitrate series. An examination of a large scale plot of figure 1 shows that for solution 5 the point which represents the solubility of lead bromate falls considerably below the best smooth curve through the experimental points; the same thing is observed to a slighter degree in the case of solution 3 ($C_s = 0.01116$).

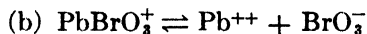
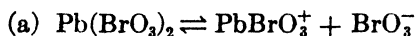
We were not so successful in dealing with the lead nitrate series except when the concentration of added lead nitrate was very small. When a large excess of lead nitrate is present, our results seem to indicate that not only does an appreciable fraction of the added lead ions combine with BrO_3^- to form PbBrO_3^+ , but that a considerable amount of undissociated lead bromate is also formed.

SUMMARY

1. We have determined the solubility at 25°C. of lead bromate in pure water and in the presence of potassium nitrate, sodium nitrate, lithium nitrate, calcium nitrate, strontium nitrate, and lead nitrate.

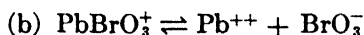
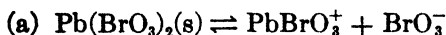
2. The theory of Debye and Hückel is not valid for these solutions if we assume that lead bromate exists in solution as Pb^{++} and BrO_3^- exclusively.

3. We postulate that the ionization of lead bromate occurs in two stages



Of these we assume that the first is virtually complete and that the second is incomplete.

4. These assumptions, when incorporated into the equations of Debye and Hückel, enabled us to determine certain equilibrium constants related to the reactions



5. Consistent values of K_1 and K_2 were found by a study of the potassium nitrate, sodium nitrate, and lithium nitrate solutions. Using these values of K_1 and K_2 , satisfactorily constant values of the parameter A were calculated for both the calcium nitrate and the strontium nitrate series.

6. The stoichiometric activity coefficient of lead bromate for any of the solutions listed can be easily calculated from the value of K_1 . Other activity coefficients are given in the tables.

REFERENCES

- (1) BÖTTGER, W.: *Z. physik. Chem.* **46**, 577 (1903).
- (2) DEBYE, P., AND HÜCKEL, E.: *Physik. Z.* **24**, 185 (1923).
- (3) HÜCKEL, E.: *Physik. Z.* **26**, 93 (1925).
- (4) MACDOUGALL, F. H.: *J. Am. Chem. Soc.* **52**, 1390 (1930).
- (5) RAMMELSBERG, C.: *Pogg. Ann.* **52**, 84-7 (1841); *Pharm. C. B.* **12**, 256 (1841).
- (6) WATSON, F. J.: *Soc. Chem. Ind. Victoria, Proc.* **32**, 679 (1932); *Chem. Abstracts* **27**, 476 (1933).

THE SOLUBILITY OF LANTHANUM IN MERCURY FROM 0°C. TO 50°C.¹

W. GEORGE PARKS AND JOSEPH L. CAMPANELLA

Department of Chemistry, Rhode Island State College, Kingston, Rhode Island

Received September 26, 1935

INTRODUCTION

The purpose of this investigation was to determine the solubility of lanthanum in mercury from 0° to 50°C. The need for these data arose in the continuation of an investigation (17) of the theory of Debye and Hückel (5) as extended by Gronwall, LaMer, and Sandved (9) for symmetrical valence type electrolytes and by Gronwall, LaMer, and Greiff (8) for the unsymmetrical types. To test the predictions of the theory for the unsymmetrical high valence type electrolytes by employing free energy measurements obtainable from suitable galvanic cells, lanthanum salts appear to be the most promising. The more common trivalent metal salts such as those of iron and aluminum are extensively hydrolyzed in aqueous solution and therefore undesirable for E.M.F. work.

If the temperature coefficients of the electromotive force are also determined, the partial and integral heats of dilution of the salt may be computed. It is therefore desirable to have the solubility of lanthanum in mercury over the temperature range to be studied. A heterogeneous amalgam is desirable, for then the electrode is easily reproducible without analysis. No data could be obtained in the literature concerning the solubility of lanthanum in mercury except the single statement of Müller (20) that amalgams containing only 1 atomic per cent lanthanum still showed a solid phase. A gravimetric rather than an electrometric method was employed, because even though Müller found a 1 per cent amalgam to be heterogeneous he did not approach a constant E.M.F. until he employed an approximately 5 per cent amalgam. The discrepancy indicated by these observations will be investigated in future work.

The composition of the solid phase in equilibrium with the amalgam at 25°C. was investigated by chemical analysis.

PREPARATION OF MATERIALS

Mercury. Redistilled mercury was stirred under a dilute nitric acid-mercurous nitrate solution for three days. It was then redistilled three

¹ This paper is based upon a thesis submitted by Joseph L. Campanella to the Faculty of Rhode Island State College in partial fulfillment of the requirements for the degree of Master of Science in Chemistry, June, 1933.

times in a slow current of air as recommended by Hulett (12), and finally distilled once under high vacuum.

Oxalic acid. The best grade of c.p. oxalic acid was recrystallized three times from distilled water, and the crystals were dried in air.

Lanthanum. c.p. metallic lanthanum prepared by the electrolysis of the fused chloride was obtained. The metal was analyzed by precipitating the oxalate with oxalic acid and igniting to the oxide at 800–850°C. as recommended by Kolthoff and Elmquist (16). The average of two separate determinations showed 99.97 per cent lanthanum. The arc spectrum of this metal was examined in a quartz spectrograph in the laboratory of Professor W. A. Noyes, Jr., at Brown University and found to be exceptionally pure, containing only a trace of iron and aluminum. No further purification was attempted on account of the difficulties involved.

Absolute ethyl alcohol. Commercial 95 per cent alcohol was refluxed for several hours with sufficient lime to remove 10 per cent water and then distilled, discarding the initial and final 200-cc. portions. The middle portion was again distilled from sufficient metallic sodium to remove an additional 5 per cent of water. Density determinations showed the alcohol thus prepared to be 99.89 per cent pure (14).

Lanthanum bromide monohydrate. To a 10 per cent solution of lanthanum chloride which showed no absorption lines in the visible spectrum (the most likely impurities cerium, neodymium, and praseodymium all possess prominent absorption lines in the visible spectrum), an excess of a 5 per cent solution of oxalic acid was added. The precipitated lanthanum oxalate was washed free from hydrochloric acid and ignited to the oxide in a large platinum dish. The oxide was dissolved in c.p. hydrobromic acid; on slow evaporation the solution furnished colorless crystals of heptahydrated lanthanum bromide. The monohydrate was prepared by long dehydration (ten to twelve days) of the more highly hydrated salt *in vacuo* at 90°C. The composition was checked by chemical analysis. The experimental and theoretical values for lanthanum checked to ± 0.19 per cent. Temperatures above 90°C. can not be employed because of the formation of insoluble basic compounds (16).

Propylenediamine. Propylenediamine (70–75 per cent) was obtained from the Eastman Kodak Company for the determination of mercury by the method of Spacu and Spacu (25).

EXPERIMENTAL PROCEDURE

The high basicity of lanthanum makes the amalgam very reactive in air and water. This eliminates the electrolytic method of formation of both the metal and its amalgams in aqueous solutions. The amalgams have been prepared with a fair degree of success by the electrolysis of concentrated solutions of $\text{LaBr}_3 \cdot \text{H}_2\text{O}$, LaCl_3 , or $\text{LaCl}_3 \cdot \text{H}_2\text{O}$ in absolute ethyl

alcohol (2, 15, 18). The amalgams employed in this investigation were prepared by two methods: (1) The necessary amounts of lanthanum and mercury to make 0.5 per cent, 1 per cent, 2 per cent, and 3 per cent amalgams were weighed out separately and put into a fused quartz flask. The flask was evacuated, and then heated in an oil bath to approximately 200°C. for eight hours. The lanthanum had by this time disappeared, and a pasty two-phase amalgam resulted. The same phenomenon that Müller (20) reported with respect to the pasty solid phase was observed in all cases. However, this behavior seemed to have no effect on the composition of either the liquid or solid phase. (2) Electrolysis of a concentrated solution of $\text{LaBr}_3 \cdot \text{H}_2\text{O}$ in absolute ethyl alcohol, as recommended by Audrieth and coworkers (2, 15, 18), was the second method employed. A solution of 9 g. of $\text{LaBr}_3 \cdot \text{H}_2\text{O}$ in 25 cc. of absolute ethyl alcohol was used in a test tube type cell having a platinum contact sealed in the bottom. The mercury forming the cathode was slowly stirred by an air-tight stirrer. A current of 0.2 of an ampere per square centimeter was passed through the solution for twenty to twenty-four hours. The cell was cooled continuously by running water.

The heterogeneous amalgam prepared by either method was placed in a fused quartz flask (50-cc. capacity) and evacuated. The flask was placed in a water thermostat at $25 \pm 0.01^\circ\text{C}$. and shaken at intervals for several days. After reaching equilibrium, which was approached from both sides, the flask was opened and samples of the liquid phase withdrawn for analysis by means of a special filter pipet. This pipet was a modified form of that used by Hulett and de Lury (13) in their work on cadmium amalgam. The details of this pipet are shown in figure 1. By means of a vacuum pump attached at B the amalgam was drawn into C through the tight plug of glass wool, A. The filtered amalgam was dropped into a small container and quickly closed for weighing. A supply of these pipets was kept in the thermostat so that they would be at the proper temperature. This method of separating the two phases is considered superior to filtering through chamois leather or sintered Jena glass crucibles, because it is more rapid. With lanthanum amalgams this is important on account of their rapid oxidation in air. Furthermore, Russell (24) found the use of chamois skin unreliable.

After removing the samples at one temperature the next temperature level studied was set and the process repeated. For operating the thermostat at 12.5°C . a modified form of the apparatus recommended by Stier (26) was employed. For operation at 0°C . a bath of ice and water mush was used as described previously (17). The Beckman thermometers were checked at intervals against a standard thermometer recently certified by the Bureau of Standards.

The analysis of the samples presented some difficulty on account of the

relatively small amount of lanthanum and large amount of mercury present. None of the ordinary methods of quantitative analysis was found applicable, nor would hydrochloric acid react quantitatively with the amalgam in a special flask similar to that used by Hulett and de Lury (13). It was soon observed, as noted by other investigators (2, 15, 18, 20), that lanthanum, like aluminum, completely separates from the amalgam when left exposed to the air. The lanthanum separates as the greyish white hydroxide with some basic carbonate. Consequently after weighing the samples they were set aside in contact with the air for two weeks. To prevent the possible formation of a protective coating the samples were shaken at regular intervals. At the end of this time a measured quantity of 0.1 *N* hydrochloric acid was added to the amalgam, and after standing a

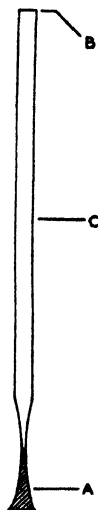


FIG. 1. Filter pipet

few minutes the excess acid determined by titration with standard carbonate-free sodium hydroxide, using phenol red as an indicator. The analytical weights and burets used were calibrated, and corrections were applied where necessary. It was found that under the conditions employed (approximately 0.1 *N* hydrochloric acid) a negligible quantity of the mercury dissolved. It is interesting to note that the samples lost weight on standing the two weeks in spite of the increase in weight due to compound formation with the oxygen in the air. This was undoubtedly due to evaporation of the mercury. This method of analysis has been found by Jukkola, Audrieth, and Hopkins (15) to check the gravimetric method of precipitation as the oxalate and ignition to the oxide. The solid phase in the amalgam at 25°C. was analyzed for both mercury and lanthanum.

After the amalgam reached equilibrium in the thermostat, the liquid and solid phases were quickly separated by filtering through a plug of glass wool. The lanthanum was determined by precipitating the oxalate with oxalic acid and igniting to the oxide. The quantity of mercury present in this case was much smaller, and its precipitation as the oxalate could be

TABLE 1
The solubility of lanthanum in mercury

<i>t</i>	WEIGHT PER CENT LANTHANUM	AVERAGE	ATOMIC PER CENT LANTHANUM
°C.			
0	0 00552 0 00540 0 00544 0 00558 0 00566	0 00552 ± 0 00008	0 00640
12 5	0 00899 0 00909 0 00913 0 00902 0 00916	0 00907 ± 0 00006	0 00934
25	0 00952 0 00949 0 00965 0 00965 0 00967	0 00960 ± 0 00006	0 0133
37 5	0 0134 0 0139 0 0138 0 0126 0 0133	0 0134 ± 0 0004	0 0182
50	0 0179 0 0190 0 0178 0 0185 0 0189	0 0184 ± 0 0005	0 0246

prevented by hydrochloric acid. The mercury was determined in the filtrate from the oxalate precipitation by the method of Spacu and Spacu, using propylenediamine (25).

RESULTS AND DISCUSSION

The solubility of lanthanum in mercury is given in table 1 for the various temperatures studied. The results tabulated represent the average of at

least four separate analyses on individual amalgams prepared by the methods previously described. The atomic per cent was calculated from the weight per cent by the graphical method given by Ölander (22) and checked by analytical computation. The results in table 1 are shown graphically in figure 2, where the log of the atomic fraction is plotted against the reciprocal of the absolute temperature. The slope of the line was determined from a large scale plot and the line corresponds to the equation

$$\log N_2 = \frac{-1020}{T} - 0.4575$$

where N_2 is the atomic fraction of lanthanum in the saturated amalgam.

The agreement between the thermal and electrolytic amalgams was not

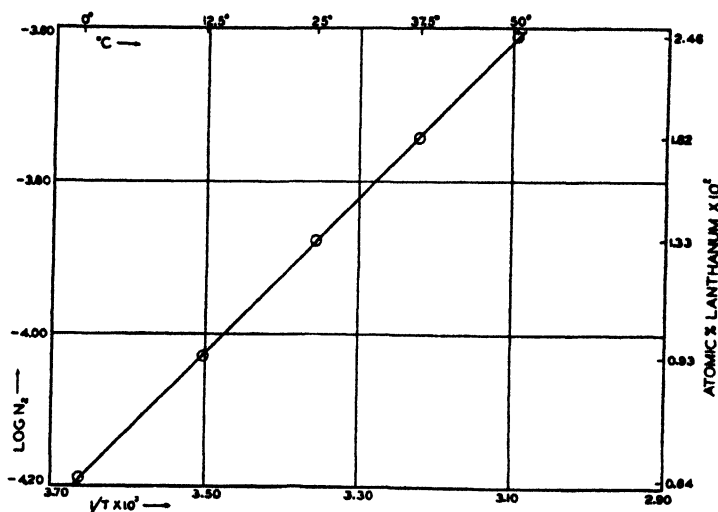


FIG. 2. The solubility of lanthanum in mercury

as good as desired. The per cent of lanthanum in the electrolytic amalgams was consistently higher than in the thermal amalgams. This discrepancy may be investigated by future work. Most of the amalgams here reported were prepared by the thermal method.

The solubility of a sparingly soluble metal in mercury is clearly not likely to be a definite quantity. Some metals, like copper and manganese and unlike zinc, lead, or tin, are known to form aggregates not only with themselves but also with mercury. It has been claimed that iron amalgams (4) and sodium amalgams (23) (up to 0.14 per cent sodium) are definitely colloidal in nature. However, in the case of liquid sodium amalgams, Bent (3) finds no evidence of a colloidal nature. The sizes of the particles in any amalgam may accordingly vary from atomic dimen-

sions upwards, and the quantity which passes through a filter would then depend upon the factors controlling the distribution of particle sizes and the diameter of the filter pores. Until the size of particles in mercury have been determined, the term "solubility" must have a limited meaning. A method other than filtration must be found for determining a homogeneous phase. This is particularly important with lanthanum amalgams on account of the peculiar pasty composition of all amalgams of low lanthanum content. The values reported at least fix the upper limit of the solubility.

In the light of the relationship between the melting point of a metal and its solubility in mercury established by Tammann and Hinnüber (27) our results are not unreasonable. They find that for metals melting at from 300° to 400°C. more than 1 per cent of the metal is soluble in mercury, and this decreases with increasing melting point. For metals melting around 1000°C. (lanthanum melts at approximately 826°C.) the solubility is 0.1 per cent and less.

The low solubility of lanthanum in mercury, together with the general properties of its amalgams, leads us to the conclusion that amalgams of this metal are unsuited for precise electromotive force measurements without considerable difficulty. The analysis of the amalgam can be eliminated by employing a two-phase system, but then a dropping electrode cannot be used and non-aqueous solvents are necessary on account of the activity of the amalgam.

These data may be interpreted in terms of internal pressures and the solubility theory as described by Hildebrand (10). According to the theory, the insolubility of lanthanum and mercury in each other should follow from their position in the table of internal pressures. However, one cannot predict the existence of compounds from internal pressures, and even though a large difference in internal pressures exists, insolubility cannot occur if compound formation takes place.

There are many ways of estimating the internal pressures of metals, but we are handicapped in the case of lanthanum because the necessary physical properties in the liquid state (such as coefficient of expansion and compressibility, surface tension, and heat of vaporization) are not known. If we adopt the method of Gilfillan and Bent (6) and divide the boiling point (19), although it is not accurately known, by the atomic volume (21), lanthanum is placed between bismuth and lead in the table as given by Hildebrand, Hogness, and Taylor (11). This position indicates a rather large difference in the internal pressure of mercury and of lanthanum (approximately 250 per cent increase) and is in accord with the insolubility found in this investigation. Furthermore, the solubility of lead in mercury has been determined by Gouy (7) and found to be 0.013 per cent by weight at 25°C. Andrews and Johnston (1) found the solubility of bismuth in

mercury to be very small. Lanthanum should be mutually soluble with lead and with bismuth. However, it should be remembered that this position for lanthanum is based on slightly inaccurate constants.

The results of the analysis of the solid phase in the amalgam at 25°C. are summarized in table 2. In each case the value given is the average of two determinations made on four separately prepared amalgams.

The empirical formula calculated for a compound having the above ratio of lanthanum to mercury is $\text{La}_2\text{Hg}_{11}$. To determine whether this compound is a chemical individual, it is necessary to determine the composition at various temperatures to see if the composition is constant and between what limits it exists. Since it is extremely difficult to separate completely the crystalline amalgam from adhering mother liquor, thereby making the analytical results uncertain, we did not attempt this problem at this time.

TABLE 2
Analysis of solid phase in lanthanum amalgam at 25°C.

WEIGHT PER CENT LANTHANUM	WEIGHT PER CENT MERCURY
11.00 \pm 0.12	88.99 \pm 0.08

SUMMARY

1. Lanthanum amalgams were prepared by direct heating of the metal with mercury and by the electrolysis of $\text{LaBr}_3 \cdot \text{H}_2\text{O}$ in absolute ethyl alcohol.

2. The solubility of lanthanum in mercury is reported at 0°, 12.5°, 25°, 37.5° and 50°C.

3. In the temperature range from 0° to 50°C. the solubility is represented by the equation:

$$\log N_2 = \frac{-1020}{T} - 0.4575$$

4. A brief discussion of the problems affecting the determination of the solubility of a sparingly soluble metal in mercury is given.

5. The low solubility of lanthanum in mercury indicates that lanthanum has a rather high internal pressure, approximately the same as that of bismuth.

6. From the general behavior of lanthanum amalgam we believe it unsuited for precise E.M.F. work without considerable difficulty.

REFERENCES

- (1) ANDREWS AND JOHNSTON: J. Inst. Metals **32**, 385 (1924).
- (2) AUDRIETH, JUKKOLA, MEINTS, AND HOPKINS: J. Am. Chem. Soc. **53**, 1805 (1931).
- (3) BENT: J. Phys. Chem. **37**, 431 (1933).

- (4) CHUIKO: Ukrain. Khem. Zhur. **6**, No. 5-6, Sci. Part., 229 (1931).
- (5) DEBYE AND HÜCKEL: Physik. Z. **24**, 185 (1923).
- (6) GILFILLAN AND BENT: J. Am. Chem. Soc. **56**, 1661 (1934).
- (7) GOUY: J. phys. [3] **4**, 320 (1895).
- (8) GRONWALL, LAMER, AND GREIFF: J. Phys. Chem. **35**, 2245 (1931).
- (9) GRONWALL, LAMER, AND SANDVED: Physik. Z. **29**, 358 (1928).
- (10) HILDEBRAND: Solubility, p. 180 et seq. The Chemical Catalog Co., Inc., New York (1924).
- (11) HILDEBRAND, HOGNESS, AND TAYLOR: J. Am. Chem. Soc. **45**, 2830 (1923).
- (12) HULETT: Phys. Rev. **21**, 388 (1905); **33**, 307 (1911).
- (13) HULETT AND DE LURY: J. Am. Chem. Soc. **30**, 1805 (1908).
- (14) International Critical Tables, Vol. III, p. 116. The McGraw-Hill Book Co., New York (1929).
- (15) JUUKOLA, AUDRIETH, AND HOPKINS: J. Am. Chem. Soc. **56**, 303 (1934).
- (16) KOLTHOFF AND ELMQUIST: J. Am. Chem. Soc. **53**, 1225 (1931).
- (17) LAMER AND PARKS, W. G.: J. Am. Chem. Soc. **53**, 2040 (1931); **55**, 4343 (1933).
- (18) MEINTS, HOPKINS, AND AUDRIETH: Z. anorg. allgem. Chem. **211**, 237 (1933).
- (19) MOTT: Trans. Am. Electrochem. Soc. **34**, 287 (1918).
- (20) MÜLLER, R.: Monatsh. **53**, 215 (1929).
- (21) MUTHMANN AND WEISS: Ann. **331**, 1 (1904).
- (22) ÖLANDER: Ind. Eng. Chem., Anal. Ed. **4**, 438 (1932).
- (23) PARANJPE AND JOSHI: J. Univ. Bombay **1**, Pt. 2, 17 (1932).
- (24) RUSSELL: J. Chem. Soc. **1932**, 835, 891.
- (25) SPACU AND SPACU: Z. anal. Chem. **89**, 188 (1932).
- (26) STIER: Science **73**, 288 (1931).
- (27) TAMMANN AND HINNÜBER: Z. anorg. allgem. Chem. **160**, 242 (1927).

X-RAY STUDIES OF CRYSTALLITE ORIENTATION IN CELLULOSE FIBERS. II

SYNTHETIC FIBERS FROM BACTERIAL CELLULOSE MEMBRANES¹

WAYNE A. SISSON²

Department of Chemistry, University of Illinois, Urbana, Illinois

Received September 25, 1935

As partial proof for the conclusions drawn in a previous paper (13), x-ray diagrams of natural fibers were compared with those of fibers synthesized from bacterial cellulose membranes. During the preparation of these "synthetic fibers," certain interesting observations regarding the plastic behavior of the crystallite suggested a further study of the type and degree relationship between deformation and orientation. It is the purpose of the present paper to describe briefly this extended investigation and especially to point out the significance of the results in that they appear to throw additional light on the question raised in the earlier paper (13), namely, what is the nature of the crystallite? Further information in this connection is not only of theoretical interest but also of practical importance, especially in the production of regenerated cellulose sheets and fibers.

Aside from a study of the characteristics of cellulose fiber diagrams themselves—a critical review of which has been given elsewhere (14)—one of the useful methods of investigating the configuration of the crystallite is to observe with x-rays its plastic behavior. Unfortunately, owing to the existence of a complex, ever varying, cylindrical cell wall, harboring numerous non-cellulosic materials, it is extremely difficult to draw definite conclusions when the method is applied to natural fibers. Although bacterial cellulose membranes have little macroscopic resemblance to natural fibers, they offer a unique opportunity for studying certain fundamental problems relating to the fine structure of natural cellulose for the following reasons: (1) they possess a well-formed, natural cellulose, crystalline structure; (2) they exist as a uniform membrane in a highly swollen or gel condition; (3) plastic flow can be readily produced in the

¹ Presented before the Division of Cellulose Chemistry at the Eighty-ninth meeting of the American Chemical Society, held in New York City, April 22-26, 1935.

² Senior Textile Foundation Fellow. Now Associate Cotton Technologist, Division of Cotton Marketing, Bureau of Agricultural Economics, U. S. Department of Agriculture, Washington, D. C.

natural membrane, while with natural fibers it is necessary to use a swelling agent first,—a process which usually changes the native to the mercerized crystalline form; and (4) the size of the membrane specimen allows a direct correlation of the x-ray and other data, while a bundle of natural fibers is necessary for a satisfactory x-ray diagram. These advantages first suggested themselves in the course of confirming with x-rays the chemical results of Hibbert and Barsha (3) regarding the identity of membrane and cotton cellulose.

DESCRIPTION OF MEMBRANES

Membranes prepared by bacterial action from solutions of sucrose, glucose, glycerol, fructose, galactose, and mannitol were used.³ The method of preparing the membranes and a description of their properties may be found in the publications of Hibbert and coworkers (3, 6, 7, 17). In brief, the "membranes" are synthesized from sugar solutions by the bacterium *Acetobacter xylinus* in the presence of a nutrient medium. As deposited on the surface of the solution by the bacteria, the membranes are in a highly swollen or gel condition. They contain about 1 g. of cellulose to 100 g. of water, a large portion of which can be removed by mechanical pressure. The removal of this water, either by pressure or by drying, is an irreversible process, and the dried membranes are tough dense parchments, very resistant to the penetration of liquids. The membranes are chemically identical with cotton cellulose, as shown by the methylation, acetylation, acetolysis, and hydrolysis experiments of Barsha and Hibbert (3).

Farr and Eckerson (5), from microscopic and microchemical studies, have recently found the membrane to consist of bacteria, and each bacterium to be composed of a protoplast surrounded by a relatively thick cellulose layer, which in turn is coated with a thin layer of pectic substance. They found the membrane to be built up of thin layers of these bacteria, and the uniform color obtained in polarized light (5) indicates directional arrangement of strands of bacteria in these thin layers.

DEFINITION OF TYPES OF ORIENTATION

In the majority of specimens examined there was more or less deviation from the preferred type of orientation present, but, owing to the large number of samples described, the orientation of each will not be represented by distribution curves (16) or face pole diagrams (20). Instead, the preferred orientation of each sample discussed will be classified merely as one of the following types:

Random orientation. The crystallites are arranged in all possible directions, and the same random x-ray diagram is obtained with the sample at any angle to the x-ray beam.

³ These membranes were kindly furnished by Dr. Harold Hibbert.

Uniplanar orientation. The only limitation imposed is that the b -axes (direction of cellulose chains) of the crystallites lie parallel to a plane. The crystallites lie at random in the plane and have all possible rotations around their b -axes. With the plane perpendicular to the x-ray beam, the x-ray diagram is random with all lines present; if the plane is parallel, a fiber pattern is obtained with all lines present.

*Selective uniplanar orientation.*⁴ The orientation is similar to a uniplanar orientation in that the b -axes are parallel to and are arranged at random in a plane, but differs in that the (101) planes of the crystallite have a selective orientation parallel to the plane (usually the large surface of the specimen). With the x-ray beam perpendicular to the plane, a random oriented pattern is obtained with the (101) line missing and the

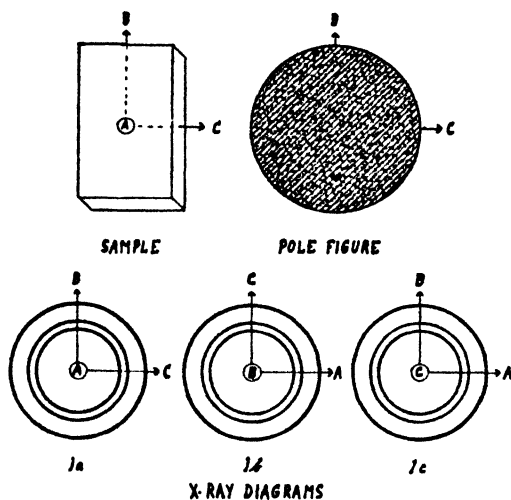


FIG. 1. Random orientation (see text for explanation)

(10 $\bar{1}$) present. With the beam parallel, the (101) line is present as a dense arc on the equator, while the (10 $\bar{1}$) is present only as a faint arc on the meridian.

Uniaxial orientation. The only limitation imposed is that the b -axes of the crystallite have a preferred orientation parallel to the fiber axis. With the x-ray beam perpendicular to the fiber axis, the (101), (10 $\bar{1}$), and (002) lines exist as intensity maxima at the equator, and their relative densities remain constant with rotation of the sample around the fiber axis as long as the fiber axis is perpendicular to the x-ray beam. If the x-ray beam is parallel to the fiber axis, a random pattern is obtained.

Selective uniaxial orientation. The b -axes of the crystallites are not only parallel to the fiber axis, but the (101) planes are also parallel to a

⁴ Often referred to as a ring fiber structure.

plane containing the fiber axis—a combination of a uniaxial orientation and a selective uniplanar orientation (equivalent to a biaxial orientation for the cubic system). With the x-ray beam perpendicular to the fiber

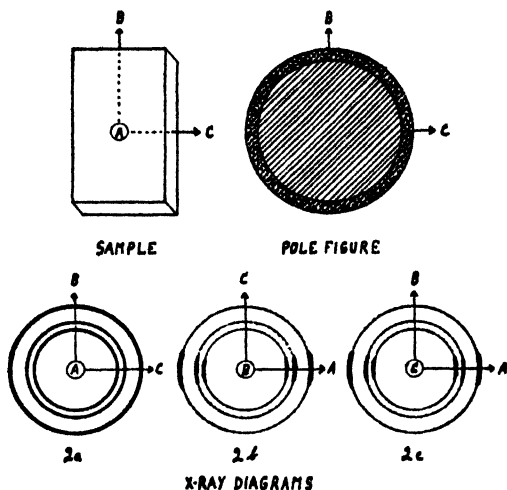


FIG. 2. Uniplanar orientation (see text for explanation)

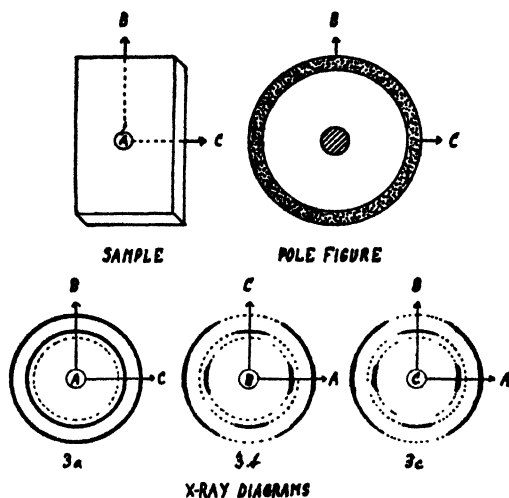


FIG. 3. Selective uniplanar orientation (see text for explanation)

axis, the (101), (10 $\bar{1}$), or (002) lines may exist as intensity maxima on the equator, but the relative densities of these lines change if the sample is rotated at different angles around the fiber axis. For example, with the selective plane parallel to the x-ray beam, the (101) line will be present

and the $(10\bar{1})$ absent; with the beam normal to the plane the order is reversed. If the fiber axis (also the plane) is parallel to the x-ray beam a fiber pattern is obtained.

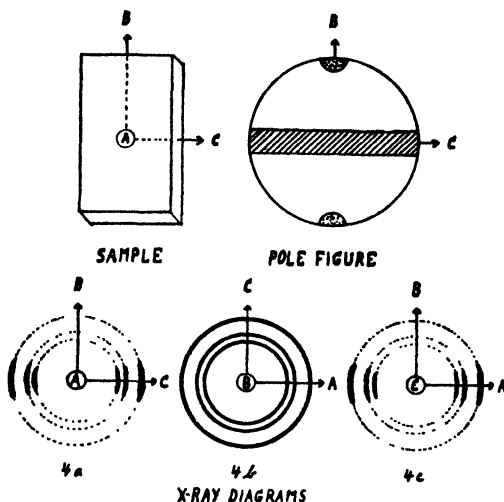


FIG. 4. Uniaxial orientation (see text for explanation)

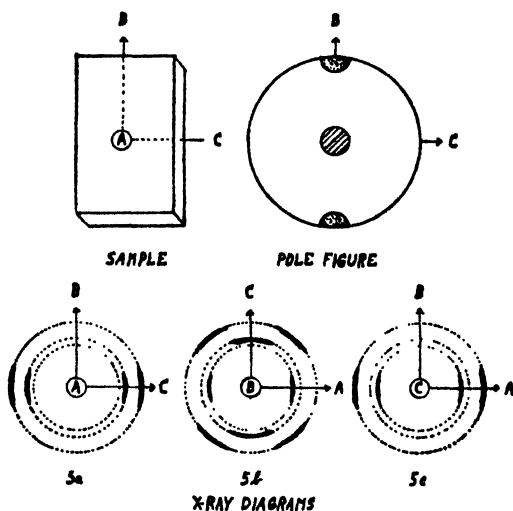


FIG. 5. Selective uniaxial orientation (see text for explanation)

Stereographic projections, or pole figures, representing the various types of orientation and their corresponding x-ray diagrams are illustrated diagrammatically in figures 1, 2, 3, 4, and 5. In the pole figures the dotted areas represent the projection of the b -axes and the cross-hatched

areas the projection of the [101] directions. A, B, and C represent arbitrary reference axes within the sample. In drawing the x-ray diagrams considerable deviation from the preferred type is assumed.

STUDY OF MEMBRANES NOT MECHANICALLY DEFORMED

Undried membranes. Owing to the large amount of water present, it is impossible to study with x-rays the orientation of the cellulose as it exists in the swollen condition. The cellulose diffraction pattern, if present, is completely masked by the characteristic water haloes, and as the sample dries the water pattern is gradually replaced by the cellulose pattern. It is not indicated from the x-ray data, therefore, whether well-defined cellulose crystallites with a definite orientation exist in the swollen membrane, or whether they are formed during drying. Microscopic observations in polarized light, however, indicate that the cellulose has a definite orientation within each bacterium and that the bacteria are arranged end-to-end to form long strands (5).

Membranes dried in the form of an aerogel. The possibility of using aerogels to study the structure and orientation of gels has been pointed out by S. S. Kistler, who kindly converted a section of the swollen membrane into an aerogel (8). The aerogel was examined with the beam perpendicular and also parallel to the plane of the membrane, and from each direction a crystalline cellulose pattern with a random orientation was obtained. If the aerogel is pressed into a sheet there is a tendency toward the formation of a selective uniplanar orientation.

Assuming the aerogeling process not to disturb the crystallinity or orientation, the random crystalline x-ray pattern would seem to indicate that crystalline cellulose is deposited with the water held between the crystallites (intermicellar). The random orientation which changes to a selective uniplanar orientation when the aerogel is pressed would suggest a honeycomb structure with a selective orientation in the cell walls of the structure. Microscopic examination reveals no visible honeycomb structure, and it is possible that the cellulose walls of the bacteria and the space between the bacteria form the cell walls of the assumed honeycomb structure. This assumption would be in harmony with the microscopic conclusion that the cellulose has a definite orientation within each bacterium.

Dried with plane of membrane parallel to a glass plate. If a large section of the membrane is allowed to dry with the flat surface resting on a horizontal glass plate, the dried sheet peeled off and subjected to x-ray analysis, a selective uniplanar orientation is found, similar to that reported by Mark and Susich for "biosynthetische cellulose" (9). Representative diagrams with the x-ray beam perpendicular and parallel to the plane of the dried membrane are shown in figures 6a and 6b, respectively. If it is assumed that the original orientation in the swollen membrane per-

sists in the dried condition, we are led to conclude that the cellulose is deposited in the membrane with a selective uniplanar orientation more perfect than is possible from a honeycomb structure. It was noticed, however, that upon drying the membrane adheres to the glass plate and that shrinkage occurs only normal to the glass plate. For example, a swollen sheet about 0.5 cm. thick will shrink to about 0.0005 cm. (0.1 per cent of its original thickness), while the width and length remain practically constant. That this unidirectional shrinkage apparently affects the orientation is shown by the following experiment.

Dried with plane of membrane perpendicular to a glass plate. Several slices of the membrane were carefully prepared and placed side by side with the original plane of the membrane perpendicular to the glass surface. Again, as with the membrane parallel, shrinkage of about the same dimensions occurred only normal to the glass and a selective uniplanar orientation was obtained.

Samples were also dried with the plane of the membrane both perpendicular and parallel to a mercury surface. This procedure allowed the membrane to contact freely in all directions while drying, and in most cases an imperfect uniplanar orientation was obtained. In other samples, provided the ratio of top to edge surface was large enough to allow practically all the water to leave from the top surface, a tendency toward a selective uniplanar orientation was found. However, for samples dried on mercury, the orientation was less perfect than for similar samples dried on glass, and the membrane had a tendency to wrinkle or pucker, which made the estimation of orientation difficult.

Membrane dried not in contact with surface. If a rod-like specimen of the membrane is allowed to dry in such a way that evaporation takes place equally in all directions normal to the strip, there is an approximately equal shrinkage in all directions and a resulting slight tendency toward a uniaxial orientation. However, when the sample is allowed to contract freely upon drying, puckering makes it difficult to estimate the orientation. In some cases the samples may be classified as having a random orientation.

These results on drying would seem to indicate that the selective uniplanar orientation of a dried membrane is probably the result of stress produced by a unidirectional shrinkage resulting from the rapid removal of water from one direction only. It is well known that shrinkage is an anisotropic property with a maximum effect perpendicular to the b -axis, but the present data would seem to indicate that the direction of shrinkage is still more specific,—it occurs principally normal to the (101) planes, or in the [101] direction. Evidently, a random orientation is the equilibrium state of the swollen membrane, and if a major shrinkage occurs in one direction upon drying the (101) planes assume a position normal to that

direction. Orientation and shrinkage appear to be two dependent variables—the result of an anisotropic crystalline property—and if one is fixed the behavior of the other is limited.

In the previous paper (13) it was pointed out that the selective orientation of dried bacterial cellulose sheets is suggestive of a general mechanism of selective cellulose deposition which might be extrapolated to plant cell membranes, but the present results would seem to invalidate the suggestion. Owing to the more rigid condition of natural fibers, it is difficult to predict what influence shrinkage may have on their orientation, but the present experiments would seem to infer that it is a factor which cannot be ignored, and that it may be in part responsible for the non-selective orientation found in spiral fibers (13),—a point which should bear further investigation.

STUDY OF DEFORMED MEMBRANES

If, instead of allowing the membrane to dry on a flat surface, it is stretched, compressed, or in some way deformed during drying, various orientation effects are produced. For studying this relationship between deformation and orientation, specimens of the swollen membrane were carefully prepared, deformed in different ways, allowed to dry, and subjected to x-ray analysis at various angles and positions along the sample.

Stretched membrane. The stretching was accomplished by suspending in a vertical position a strip of the swollen membrane and applying weights attached to the lower end. The amount of tension which could be safely applied without causing rupture was small at first, but became very great as the strip dried. Both broad flat strips and narrow rod-like strips were treated in this way. Stretching in one direction produces a uniaxial orientation which is most pronounced in the rod-like samples, gradually changing toward a selective uniaxial orientation as the strips are made more sheet-like. An x-ray pattern of a rod-like sample with the beam perpendicular to the fiber axis is shown in figure 7. Its similarity to a cotton pattern is illustrated by a comparison of figures 7 and 8.

Rolled membrane. One end of a flat strip was clamped to a glass plate and the strip rolled in one direction. This process tends to produce a selective uniaxial orientation, as illustrated in figure 9.

Drawn membrane. For this experiment a set of standard diameter holes, used for determining wire gauges, sufficed for drawing dies. A tapered end of the membrane strip was started through the die, fastened to a clamp, and pulled through by applying weights to the clamp. Since twenty to forty minutes were often needed for the final passes, precaution was necessary to prevent too rapid drying of the sample. Drawing produces a uniaxial orientation which becomes more perfect with progressive passes through the die. The type of fiber structure obtained by drawing is illustrated in figure 10.

Pressed membrane. A square section of a membrane was placed between two glass plates and pressure applied. X-ray diagrams showed the sample to possess a selective uniplanar orientation, similar to that produced by allowing a sheet to dry on a glass surface.

Membrane dried with ends fixed. A rod-like strip of swollen membrane was stretched across the end of a beaker, the ends taped to the sides of the beaker, and the strip allowed to dry. The shrinkage accompanying drying causes the strip to become very taut. X-ray diagrams show a uniaxial orientation, as illustrated in figure 11.

Flat strips were prepared in the same way with the exception that the middle of the strip rested on a glass rod of 2-cm. diameter placed across the top of the beaker. This arrangement allowed the middle of the strip to be pressed against a smooth surface while under stress. Thus the section of the strip in contact with the glass rod is influenced by both a unidirectional shrinkage and a unidirectional tension acting at right angles to each other. The result was a selective uniaxial orientation for this portion of the strip, while the part not in contact with the glass rod developed only a uniaxial orientation.

The results on deformed membranes show that, in general, three types of orientation were produced. If the plastic flow takes place (a) with reference to an axis, a uniaxial orientation is obtained; (b) if with reference to a plane, a selective uniplanar orientation; or (c) if with reference to an axis and a plane, a selective uniaxial orientation.

Microscopic study. In an effort to throw further light on the nature of the plastic flow, a microscopic study was made of the deformed membranes. From the swollen membranes, by means of suitable solvents (5), it is possible to isolate the bacteria individually or in bead-like strands. These same bacteria linked together in bead-like strands with a definite uniform interior orientation, as indicated by the uniform color in polarized light, may be found in the strongly deformed membranes. Although the isolation of these unchanged bacteria cannot be accepted as definite proof, it would seem to indicate that the bacteria may move as units during plastic deformation.

STUDY OF MERCERIZED MEMBRANES

Action of sodium hydroxide. While studying the effect of substituting the water of the swollen membranes for other liquids, an unusual phenomenon concerning the action of sodium hydroxide was observed. Normally sodium hydroxide swells cellulose materials, but in the membrane it produces a shrinkage. For example, if a swollen membrane is placed in 18 per cent sodium hydroxide it begins to contract rapidly, and in about fifteen minutes the length and breadth shrink to approximately one-fourth the original dimensions, while the thickness remains practically the same. The treated sample gives a random mercerized x-ray pattern.

The failure of several salts to produce the same action would indicate that it is not an osmotic effect. The shrinkage appears to be definitely associated with a crystallographic change to the mercerized form, since the sodium hydroxide must be of sufficient concentration (above about 14 per cent) to produce a mercerized structure before any appreciable shrinkage occurs.

If the membrane is first dried on a glass plate and then treated with sodium hydroxide, it shrinks to only about two-thirds the former width and length, with a slight increase in thickness. This process tends to destroy slightly the original selective uniplanar orientation of the dried specimen. The very compact form of the dried membrane, however, makes it difficult to produce a mercerized crystalline structure.

Specimen dried, then mercerized under stress. A number of fiber specimens previously dried under stress were treated with sodium hydroxide, subjected to the same type of original stress, washed, and allowed to dry. X-ray analysis showed that, in general, the original type of orientation is not changed, but the degree of orientation becomes more perfect. Figure 12 shows the same sample as figure 11 after being replaced over the beaker and treated for a short time with sodium hydroxide. The native crystalline structure is not changed, but the fiber structure is more perfect.

FIG. 6a. X-ray diagram of membrane dried in contact with glass surface. X-ray beam perpendicular to large surface of membrane

FIG. 6b. X-ray beam parallel to surface (same sample as figure 6a)

FIG. 7. Membrane dried with tension in one direction. X-ray beam perpendicular to fiber axis (tension axis)

FIG. 8. Typical x-ray diagram of cotton fibers. X-ray beam perpendicular to fiber axis

FIG. 9. Membrane rolled in one direction. X-ray beam normal to plane and direction of rolling

FIG. 10. Membrane drawn through die. X-ray beam perpendicular to fiber axis (drawing axis)

FIG. 11. Membrane allowed to dry with ends of strip fastened to rigid supports. X-ray beam perpendicular to fiber axis (long direction of strip)

FIG. 12. Same sample as figure 11 after treatment with sodium hydroxide

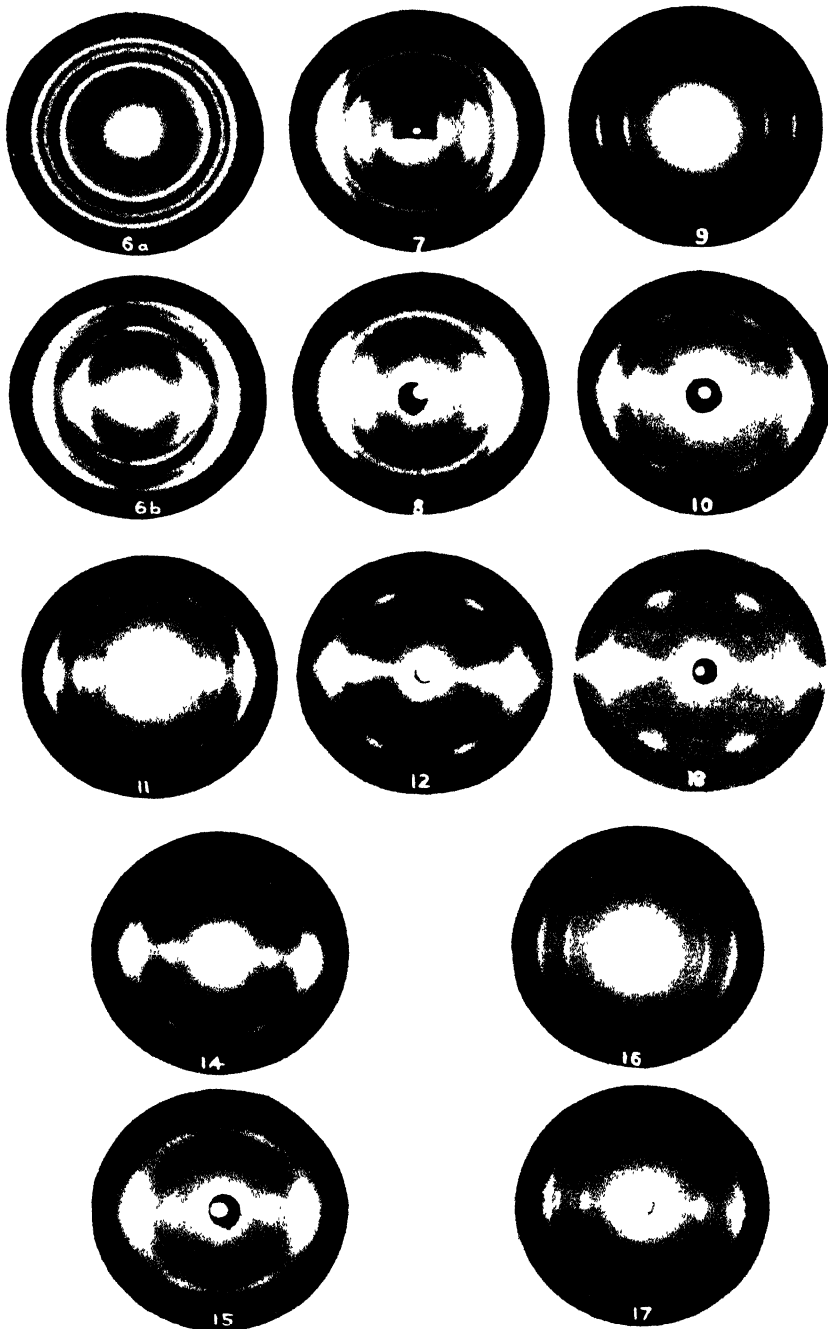
FIG. 13. Typical x-ray diagram of ramie fibers. X-ray beam perpendicular to fiber axis

FIG. 14. Strip of membrane mercerized with ends fastened to rigid supports. X-ray beam perpendicular to fiber axis (long direction of strip)

FIG. 15. Typical x-ray diagram of cuprammonium rayon. X-ray beam perpendicular to fiber axis

FIG. 16. Strip of membrane subjected to combined tension and pressure applied at right angles to each other (see text for explanation). X-ray beam perpendicular to direction of tension (axis of strip) and parallel to direction of pressure (normal to plane of strip).

FIG. 17. Same sample as figure 16 rotated 90° around fiber axis. X-ray beam still perpendicular to fiber axis (direction of tension), but perpendicular to direction of pressure (parallel to plane of strip).



FIGS 6a TO 17
353

As shown by comparison of figures 12 and 13, the fiber structure is equal to that of ramie, which is one of the most perfectly oriented natural fibers.

A number of sheets previously dried on glass were treated with sodium hydroxide and subjected to a straight tension pull. With progressive extension the selective uniplanar orientation is gradually replaced by a uniaxial orientation. At the intermediate stage both orientations may be considered as present, which results in an imperfect selective uniaxial orientation.

Specimen mercerized with ends fixed. Strips were mounted over a beaker, as previously described, and kept in contact with 18 per cent sodium hydroxide for 30 minutes, washed for 30 minutes, and allowed to dry. Owing to the shrinkage produced by the sodium hydroxide, the strips become very taut and a mercerized uniaxial fiber structure is produced, as illustrated in figure 14. Its similarity to a well oriented cuprammonium rayon diagram may be seen from a comparison of figures 14 and 15.

If the strip is placed over a glass rod and then treated with sodium hydroxide, the section in contact with the glass rod develops a selective uniaxial orientation, while that not in contact develops a uniaxial orientation.

Specimen dried, mercerized, then subjected to combined tension and compression. Uniaxial fibers, previously prepared by drawing, were placed between two smooth lead sheets and the center of the sample moistened with sodium hydroxide. The lead strips with the samples between them were then placed between a smooth steel plate and a steel rod 6 cm. in diameter. If sufficiently wide strips of lead are used and the axis of the steel rod is perpendicular to the fiber axis of the specimen, the circumference of the rod will force the lead to flow parallel to the fiber axis of the specimen when the rod and plate are pressed together by means of a large vise. Thus, simultaneously with the perpendicular pressure produced by the vise, a tension is produced in the sample by the plastic flow of the lead. Spreading of the sample is prohibited by placing thin lead strips on either side. The principle of the process has been successfully used to prepare selective uniaxial oriented specimens of keratin (1), and it is commonly used to draw a thin wire or roll a thin sheet by placing the sample inside of another metal. If thick lead sheets are used a uniaxial orientation may be obtained. However, by proper regulation of the lead thickness, the pressure, etc., specimens may be prepared by this method which show a selective uniaxial orientation, as shown by figures 16 and 17 with the x-ray beam perpendicular and parallel to the flat side of the sample, respectively (x-ray beam perpendicular to the fiber axis). The presence of a selective uniaxial orientation was further confirmed by a fiber pattern when the x-ray beam was made parallel to the fiber axis.

This experiment illustrates the fact that it is possible, by the proper

combination of tension and pressure, to prepare a selective uniaxial orientation by forcing the sample to become longer and thinner but not broader or narrower,—a change in dimensions corresponding to that of a rolled sheet metal. The experiment indicates also the possibility of preparing a specimen with an orientation approaching that of a single crystal, from which the relative refractive indices along the a - and c -axes may be obtained, as well as other fundamental crystallographic information heretofore unattainable, owing to the absence of single crystals of cellulose.

THEORETICAL

In connection with the selective orienting properties of the crystallite, it is interesting to note that the (101) crystallographic plane of cellulose, in its influence on the type of orientation obtained, appears to play a rôle analogous to that of a glide plane in metals. The mechanism of obtaining the orientation, however, must be quite different for the two materials. Instead of a glide plane slip as for metals, all of the evidence points to a "micellar flow" or movement of the crystallite as a unit for cellulose (14). The equilibrium position for the cellulose crystallite, therefore, must be governed, not by the symmetry of glide planes, but by the external configuration of the crystallite.

The pronounced orienting tendency of cellulose with reference to the b -axis—that a rayon filament can be oriented, for example, by stretching—is well known, and this property is usually attributed to rod-like micelles or fibrous bundles of cellulose chains which are oriented parallel to the direction of stretching. If an elongated shape in the direction of the b -axis is responsible for the parallel alignment of the crystallites when cellulose is stretched, the question then arises, what configuration of the crystallite is responsible for the selective orienting tendency with reference to the (101) plane?

Assuming an elongated cellulose crystallite which moves as a unit during plastic flow, there are two possible external configurations which could account for its selective behavior: (1) it could have a flat or ribbon-like shape, or (2) it could have a greater secondary valence attraction on two sides. In other words, the selective orienting tendency of the crystallites may be due either to their shape or to the cohesive forces between them, or perhaps to a combination of both factors.

It is impossible to predict to what extent cleavage planes may exist in crystalline cellulose, but from analogy to other crystals one would expect a tendency toward cleavage along the (101) planes. If this were true then the conditions would be favorable for the existence of flat or shingle-like crystallites, which, owing to their shape, should behave in the manner experimentally observed.

If it is shape alone that is responsible for the selective orienting tendency

of cellulose, then we have reason to believe that the crystallite would have to be rather ribbon-like. In the case of superpolymers, Carothers (4) has estimated that the molecular weight should be above 12,000 and the

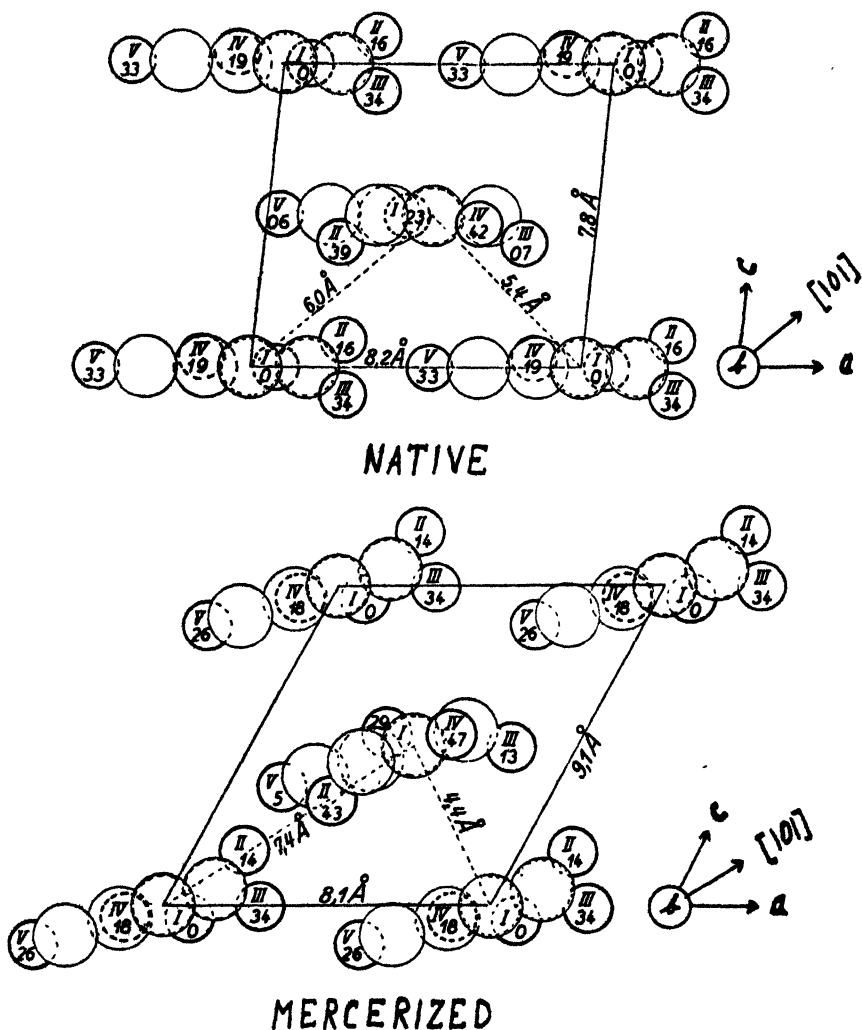


FIG. 18a and 18b. View down the *b*-axis of the cellulose unit cell (after K. R. Andress: *Z. physik. Chem.* 4B, 190 (1929))

molecular length above 1000 A.U. before orientation can be produced easily by stretching. On the other hand, oriented films may be produced readily from comparatively short molecules, a property due to the exist-

ence of polar groups at the ends of the molecules, and it would seem logical to assume that the polar hydroxyl groups of cellulose may be partly responsible for the orienting properties of cellulose.

As may be seen from figure 18a, the (101) planes of cellulose have the largest number of hydroxyl groups per square unit of surface. Since the secondary valence of cellulose is attributed to hydroxyl groups, the sides of the crystallite parallel to the (101) planes should have the greatest valence forces, owing to the geometrical arrangement of the glucose residues in the crystal lattice, and these hydroxyl groups may assist the selective orienting tendency of the crystallite. In addition to their selective orienting tendency, these hydroxyl groups, and also the ones at the ends of the cellulose chains, should assist the orienting tendency with reference to the *b*-axis.

The selective orienting tendency is not a unique property of bacterial cellulose membranes. Gelatin (18), myosin (2), cellulose acetate and cellulose nitrate films (10), and regenerated cellulose films (15) all show a selective uniplanar orientation when allowed to dry in sheet form. Keratin (1), regenerated cellulose films (15), and cellulose acetate and cellulose nitrate films (10) also show a selective uniplanar or uniaxial orientation when treated under the proper conditions, and it is interesting to note that all of these materials which show a selective orienting tendency have polar groups attached to fibrous molecules which exist as elongated micelles or crystallites.

There are several properties of cellulose which are in harmony with the concept of hydroxyl group influence. For example, since the hydroxyl groups are largely responsible for the sorption of water by cellulose (12), a crystallite studded with hydroxyl groups on two sides would be expected to have a major shrinkage normal to the (101) planes. Furthermore, since the (101) planes of the mercerized lattice have more (about 25 per cent) available hydroxyl groups per unit of surface than the native, as may be seen from a comparison of figures 16a and 18b, this may account in part for the greater sorption of water by mercerized cellulose and its greater selective orienting tendency.

DISCUSSION AND SUMMARY OF RESULTS

In general, the experimental results would lead one to conclude that the major factor in determining the type and degree of orientation found in deformed membranes is the relative direction and extent of the flow, or change in dimensions of the sample, rather than the nature, magnitude, or direction of the forces producing the flow. In other words, *if the sample is elongated in one direction, the b-axes of the crystallites are oriented parallel to that direction; if the sample is constricted in one direction, the (101) planes are oriented normal to that direction.* This general

rule would seem to apply to both mercerized and unmercerized membranes, regardless of whether the changes in dimensions are produced by shrinkage or by plastic flow due to mechanical force. It appears less difficult, however, to prepare a selective oriented fiber structure from the mercerized than from the unmercerized membranes.

This rule is not suggested as a rigid law for the plastic behavior of all cellulose materials—it is merely an attempt to generalize the behavior of the samples investigated—but preliminary results indicate that it may be of general application, and it is interesting to note that a similar rule may be applied to the plastic flow of metals (11). It appears to be in agreement with the optical results of McNally and Sheppard (10) on cellulose nitrate and cellulose acetate films, and with the x-ray results of Trillat (19) on cellulose esters.

Although it is tentatively suggested that polar groups, as well as shape, may influence the selective orienting properties of cellulose, the present results are not conclusive either as to the shape and size of the membrane crystallite, or as to the exact cause of its orienting tendencies. It is tempting to assume that part of the orientation effects are due directly to cell distortion, or to the flattening of a honeycomb structure. Careful observation, however, indicates that it is necessary to invoke something beyond cell distortion; the orienting tendency of cellulose appears to be a fundamental property, present not only in native, but also in regenerated and cellulose derivatives where a cell structure cannot be assumed. As pointed out before, there is some evidence that bead-like strands of bacteria move as units during plastic flow, but the evidence is not conclusive. The unit may be considerably smaller, and it is difficult to predict at what crystallite dimensions the influence of shape or polar groups would begin to have an orienting effect. The major point which *the present results emphasize* in this connection is that, whatever the final concept of the membrane crystallite may be, this concept must take into consideration the fact that *the crystallite possesses a major orienting tendency with reference to the b-axis, and a minor or selective orienting tendency with reference to the (101) plane.*

The author wishes to express his gratitude to Professor G. L. Clark for his interest and support, and to Professor Harold Hibbert for furnishing the necessary membrane samples.

REFERENCES

- (1) ASTBURY, W. T., AND SISSON, W. A.: *Proc. Roy. Soc. London.* **150A**, 533 (1935).
- (2) ASTBURY, W. T., AND DICKINSON, SYLVIA: *Nature* **135**, 95 (1935).
- (3) BARSHA, J., AND HIBBERT, HAROLD: *Can. J. Research* **10**, 170 (1934).
- (4) CAROTHERS, W. H., AND HILL, J. W.: *J. Am. Chem. Soc.* **54**, 1579 (1932).
- (5) FARR, W. K., AND ECKERSON, S. H.: *Contrib. Boyce Thompson Inst.* **6**, 189 (1934).

- (6) HARRISON, F. C., TARR, H. L. A., AND HIBBERT, HAROLD: Can. J. Research **3**, 449 (1930).
- (7) HIBBERT, HAROLD, AND BARSHA, J.: Can. J. Research **5**, 580 (1931).
- (8) KISTLER, S. S.: J. Phys. Chem. **36**, 52 (1932).
- (9) MARK, H., AND SUSICH, G. V.: Z. physik. Chem. **4B**, 431 (1929).
- (10) McNALLY, J. G., AND SHEPPARD, S. E.: J. Phys. Chem. **34**, 165 (1930).
- (11) NORTON, J. T., AND HILLER, R. E.: Trans. Am. Inst. Mining Met. Engrs. **99**, 190 (1932).
- (12) SHEPPARD, S. E.: Trans. Faraday Soc. **29**, 77 (1933).
- (13) Sisson, W. A.: Ind. Eng. Chem. **27**, 51 (1935).
- (14) Sisson, W. A.: Textile Research **5**, 119 (1935).
- (15) Sisson, W. A.: Unpublished results.
- (16) Sisson, W. A., AND CLARK, G. L.: Ind. Eng. Chem., Anal. Ed. **5**, 296 (1933).
- (17) TARR, H. L. A., AND HIBBERT, HAROLD: Can. J. Research **4**, 372 (1931).
- (18) TRILLAT, J. J.: J. chim. phys. **29**, 1 (1932).
- (19) TRILLAT, J. J.: Compt. rend. **197**, 1616 (1933).
- (20) WEVER, F.: Z. Physik **28**, 69 (1924).

THE INFLUENCE OF DENATURATION ON THE SPREADING OF PROTEINS ON A WATER SURFACE

HANS NEURATH

The Sir William Ramsay Laboratories of Inorganic and Physical Chemistry, University College, London, England

Received July 29, 1935

This paper describes observations on the effect of denaturation, by heat and by irradiation with ultra-violet light, on the spreading of aqueous solutions of ovalbumin and serum albumin on water. The term "denaturation" is somewhat loosely used to describe various changes in proteins, which lead to diminished solubility in water; thus besides the changes produced by heat and by ultra-violet light, Ramsden (15) and du Nouy (4) found that adsorption at the air-water surface produces insolubility of proteins and termed this also "denaturation." When proteins are spread on the surface of aqueous solutions they also usually become insoluble.

The numerous papers published in recent years on the spreading of proteins on a water surface (5, 6, 7, 8, 10, 11, 16) have led to the conclusion that a fully spread film of a protein at a water-air surface has the peptide chains of the protein molecules stretched out along the surface with the lyophilic groups towards the water. Serum albumin and ovalbumin show remarkable differences in their colloidal properties in bulk solution, and it was thought that a study of their power of spreading at a surface, before and after denaturation in bulk, would throw light on the nature of the denaturation process and show also whether there is an important difference in the processes of so-called "denaturation" by heat and by spreading out on a surface.

EXPERIMENTAL

Preparation of the protein solutions

Ovalbumin solutions were prepared from fresh hens' eggs by separating the yolk, diluting the white with distilled water, and filtering off the precipitated globulins; the filtrate was electrodialedyzed in Pauli's apparatus (13) for several days, the voltage being gradually increased from 5 to 220 volts. After seven days' electrodiaalysis the conductivity had reached its minimum value of 6.5×10^{-6} mhos, with 2 per cent protein solutions.

Serum albumin was prepared from defibrinated horse serum, by freeing from globulins by adding ammonium sulfate to one-third saturation,

filtering, again adding ammonium sulfate to two-thirds saturation, and electro dialyzing as with ovalbumin. The final conductivity was 4.5×10^{-6} mhos, at 2 per cent. The pH of the purified solutions was 4.80 for the ovalbumin and 4.85 for the serum albumin, measured with a quinhydrone electrode.

All solutions were kept in the ice chest at about 2°C., under a thin layer of a paraffin-toluene mixture to prevent infection. The concentration of the 2 per cent solutions was determined every few days by drying 2 cc. at 108°C. for twenty-four hours; the solutions for spreading were about one-hundredth of this concentration and were prepared from the stronger solutions by diluting with conductivity water.

Measurements of the surface pressure of the spread films

The apparatus of Adam and Jessop (2) was used. The films were frequently examined by the dark-ground illumination introduced by Zocher and Stiebel (19), with the simplifications used by Adam (1). The pH of the aqueous solutions, upon which the proteins were spread, was regulated by Walpole acetate buffers of $N/20$ or $N/300$ concentration in acetate; a brass trough was used, and the temperature regulated by an electrical heater below the trough.

The proteins were spread from aqueous solution, using Gorter's method (6, 7, 8), with but slight modifications. An Agla micrometer syringe, capable of being read to 0.0001 cc., was held horizontally close to the surface, and a measured quantity of the liquid, about 0.25 cc., expelled. It was found that if the height of the tip of the syringe was varied between 2 and 5 mm. above the water, the same results were obtained; if, however, it was brought so close to the surface that the issuing drops actually touched the water in the trough before being detached, the spreading was less complete. Every result quoted below is the mean of several measurements, which usually agreed within 1 per cent.

RESULTS

Figure 1, curves I to III, shows the surface pressure-area curves obtained with egg albumin on the buffer solutions of pH 4.8 (the isoelectric point) and 4.4. The areas were observed to increase with time slightly, owing to the spreading or unfolding of the molecule taking place slowly, up to about seven minutes. The values given are at about seven minutes after putting the material on the surface. The spreading was greater on the solution at the isoelectric point than on the more acid solution, in accordance with the findings of Gorter; it was also considerably greater on the more concentrated acid buffer than on the more dilute. Svedberg's values for the molecular weight, i.e., 34,500 for ovalbumin and 69,000 for serum albumin, were used (17, 18). No signs of inhomogeneity in the

film could be detected on the two $N/20$ buffer solutions with the dark-ground illumination below 18 dynes at 4.8 and 15 dynes at 4.4 pH, at which pressures collapse commenced. The films showed slight signs of inhomogeneity at all pressures on the dilute buffer; considerable collapse occurred on this solution at 13 dynes.

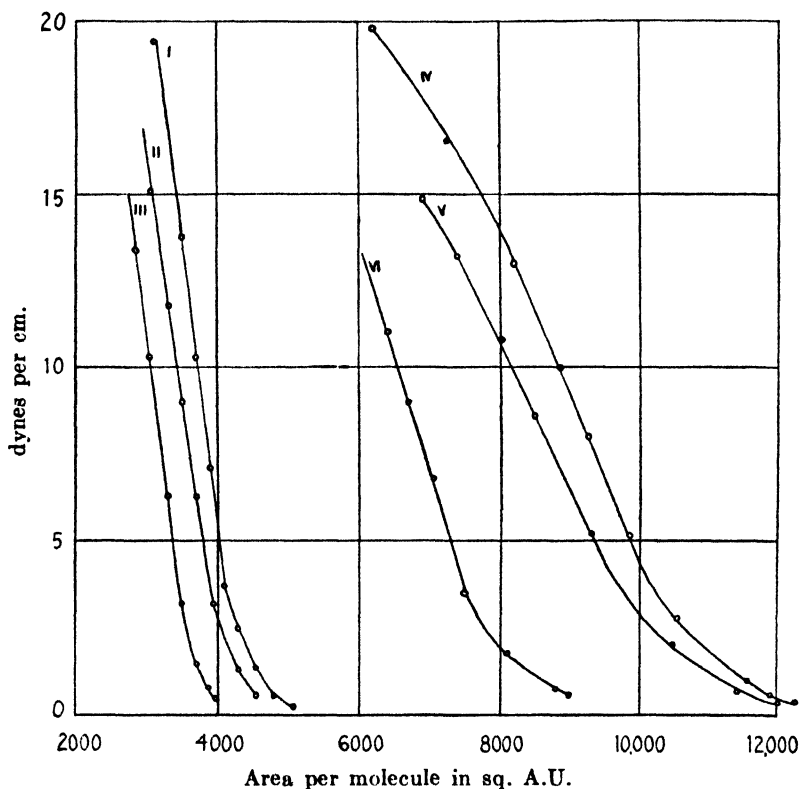


FIG. 1. Spreading of natural ovalbumin and serum albumin. Curve I, ovalbumin, pH 4.8, on $N/20$ acetate buffer, pH 4.8; curve II, ovalbumin, pH 4.4, on $N/20$ acetate buffer, pH 4.4; curve III, ovalbumin, pH 4.4, on $N/300$ acetate buffer, pH 4.4; curve IV, serum albumin, pH 4.8, on $N/20$ acetate buffer, pH 4.8; curve V, serum albumin, pH 4.4, on $N/20$ acetate buffer, pH 4.4; curve VI, serum albumin, pH 4.4, on $N/300$ acetate buffer, pH 4.4.

With serum albumin (curves IV to VI) very similar results were obtained; the velocity of spreading was somewhat less on the dilute acid buffer, and the curve refers to twelve minutes after the material was put on.

With the dark-ground illuminator, the films on the $N/20$ buffers were apparently homogeneous, and that on the dilute buffer slightly inhomogeneous; collapse occurred at 13 to 14 dynes in curve IV, at 11 to 12 dynes in curve V, and at 10 dynes in curve VI.

The films all became solid at about 3 dynes compression; this is the phenomenon described by Hughes and Rideal as "gelation" of the films.

The fully spread ovalbumin films tend to a limiting area of about 5000 sq. A.U. per molecule, or 0.88 sq. meter per milligram, in good agreement with Gorter's value of 0.9 sq. meter per milligram. This area is decidedly

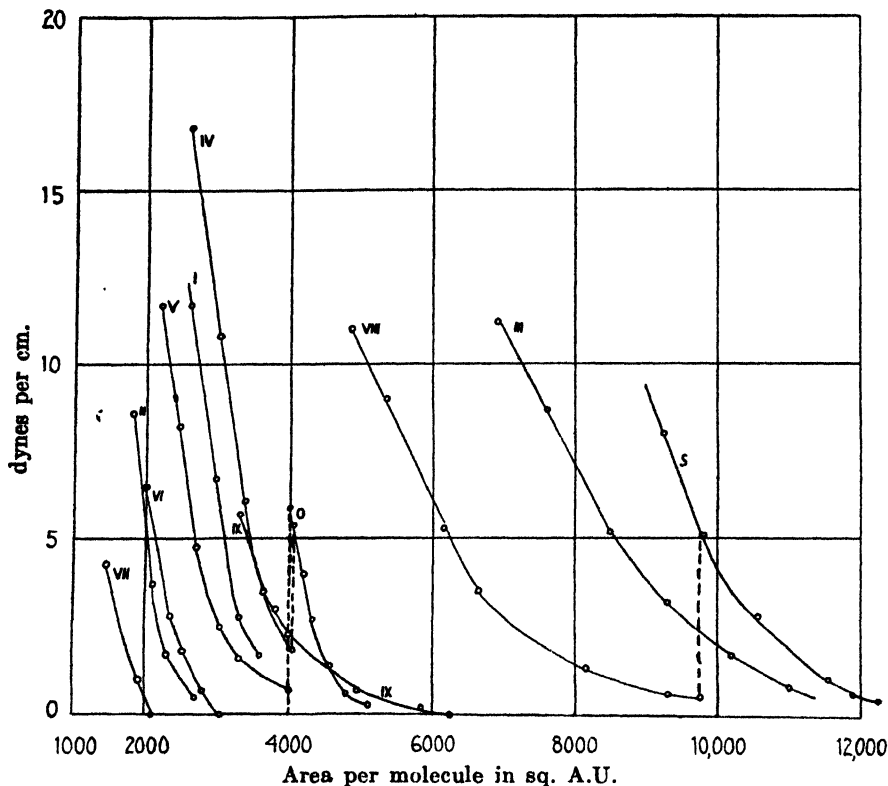


FIG. 2. Irradiation of proteins with ultra-violet light. Curve O, ovalbumin without irradiation; curve S, serum albumin without irradiation; curve I, ovalbumin, 15 minutes before spreading; curve II, ovalbumin, 70 minutes before spreading; curve III, serum albumin, 20 minutes before spreading; curve IV, ovalbumin, 3 minutes after spreading; curve V, ovalbumin, 6 minutes after spreading; curve VI, ovalbumin, 9 minutes after spreading; curve VII, ovalbumin, 20 minutes after spreading; curve VIII, serum albumin, 6 minutes after spreading; curve IX, serum albumin, 20 minutes after spreading.

larger than the maximum obtained for crystallized egg albumin by Fossbinder and Lessig (5), 3750 sq. A.U. per molecule or 0.66 sq. meter per milligram. Svedberg has shown (17), however, that crystallized egg albumin contains a fraction of molecular weight 170,000, which cannot be removed even by repeated crystallization, but is precipitated on electro-

dialysis. This would not have been present in the material used here, owing to the method of preparation. If it is assumed that the fraction of high molecular weight in crystallized egg albumin does not spread, while that of lower molecular weight spreads completely, then since Svedberg gives the average molecular weight of crystallized egg albumin as 43,000, it is easily calculated that Fossbinder and Lessig's results lead to an area per molecule for the fully spread constituent of lower molecular weight of 4950 sq. A.U., in excellent agreement with the present result and with Gorter's.

The limiting area per molecule for serum albumin is about 12,000 sq. A.U.; this value is larger than those given by Fossbinder and Lessig, but the films have been spread on solutions of very different pH.

The films give a nearly straight surface pressure-area curve above the pressure at which they become solid; the compressibility is about 70.5 sq. A.U. per dyne for egg albumin, or 1.41 per cent of the area at no compression; for serum albumin it is 250 sq. A.U. per dyne or 2.08 per cent. On decompressing the films once, there was a small amount of hysteresis, the area expanding to about 4 per cent less than before compression.

Serum albumin spreads to an area about 15 per cent larger, per gram, than ovalbumin, the area being 1.05 sq. meters per milligram.

Effects of denaturation

The dilute protein solutions (ca. 0.02 per cent) were adjusted to pH 4.4 by dilute hydrochloric acid, and heated in a quartz test tube for fifteen minutes at 100°C. The solutions were perfectly transparent after this treatment. Isoelectric solutions (pH 4.8) of the same concentration turned opaque when heated in this way; and on adding the same quantity of sulfosalicylic acid to the denatured solution and to the untreated solution, the same opacity was obtained.

On attempting to spread the heat-denatured solutions on *N*/20 or *N*/300 buffer, pH 4.4, no spreading could be obtained. No surface pressure greater than 0.3 dyne could be obtained until the area was diminished to less than one-eightieth of that at which this pressure was obtained with the natural egg albumin. The ultramicroscope showed large numbers of aggregates of different size and shape floating on the surface. Time did not promote spreading; even after twenty minutes no appreciable spreading had occurred. Incomplete denaturation, by heating for two or four minutes only, diminished the extent of spreading, but not so much as the longer heating. The spreading of both egg and serum albumin was prevented by denaturing in this way.

Denaturation by ultra-violet light was studied by irradiating the solutions before spreading in a rectangular quartz vessel of 3 mm. inside thickness at a distance of 12 cm. from a K.B.B. atmospheric quartz mer-

cury vapor lamp, 220 v., 2 amps. The pH was adjusted to 4.4. The spreading power is diminished but not entirely destroyed. Curves I and II of figure 2, were taken on spreading the solutions irradiated for 15 and 70 minutes, respectively; after 70 minutes, the solution spread to about half the area of the natural egg albumin. Twenty minutes irradiation of the serum albumin solution diminished the area of spreading only by about 10 per cent. Inhomogeneity could be detected with the dark-ground illumination on all the films spread from irradiated solutions.

The effect of ultra-violet light was also studied by irradiating the films of natural protein after spreading. The same mercury vapor lamp was used, horizontally, about 12 cm. above the surface of the water. In order to diminish the amount of contamination accidentally reaching the surface during irradiation, the films were compressed to 5 dynes. Preliminary experiments showed that, qualitatively, the effect of irradiation was the same in the uncompressed as in the compressed state. The irradiation did not raise the temperature of the interior of the solution more than 2°C.; the rise in temperature of the surface was probably not much more than this.

Curves IV to VII show the effect of increasing times of irradiation for egg albumin; curves VIII and IX, for serum albumin. During irradiation the surface pressure fell to almost nothing. The films were seen to be very homogeneous after irradiation. Irradiation on solutions of pH 4.8 and 4.4 gave similar results.

The effect seemed to be rather greater with serum albumin than with egg albumin, the areas after irradiation for 20 minutes in the spread films being about 50 per cent of the original with egg albumin and 33 per cent with serum albumin.

DISCUSSION

It is evident that the different processes known as denaturation are not all the same. The spreading of the molecules out along a surface is almost certainly an unfolding of the molecule so as to be one amino acid thick in the fully spread form, the water-attracting groups, i.e., the —CO—NH— and any free COO^- or NH_3^+ groups, being in contact with the water and the hydrocarbon chains usually oriented away from the water. The protein does not easily dissolve in the water, once it has been spread or unfolded at a surface. According to du Nouy (4), a protein in aqueous solution accumulates at the surfaces until all the protein is at the surface and none remains in the interior. Thus the unfolding of the protein molecule during its transition from interior to surface appears to be a process which occurs spontaneously, whereas the reverse process, the coiling of the unfolded molecule and its passage back from surface to interior, does not occur easily. It is probable that, when in solution in water, the protein

molecules are coiled up so that the hydrocarbon chains are buried in the interior, and the surface is covered by the water-attracting groups. Thus Ramsden's "denaturation" by shaking and adsorption at an air-water surface is probably an unfolding of the molecule.

By the action of heat, however, the transition from the coiled to the unfolded structure is practically prevented. This could arise either through an increase in the forces which bind the coiled molecule together, or by an increasing aggregation, i.e., several coiled molecules uniting. The first mechanism seems to agree best with electrochemical experience. According to Pauli (13, 14), the primary process of heat denaturation consists of an interaction between the free amino and carboxyl groups, leading to an amide-like linkage between these groups and consequently to the loss of the "zwitterion" structure. This would tend to diminish spreading for two reasons: first, because these groups would have less attraction for the water than the separate COO^- and NH_3^+ groups; second, because they would tend to bind the molecule together in the coiled-up form. Astbury (3) brings evidence that the side chain linkages between peptide chains in proteins are strengthened by denaturation; this would probably hinder the unfolding of the molecules.

Haurowitz (9) considered that denaturation consists of a breaking of the intramolecular attraction between positive and negative groups, with a loosening of the molecule by stretching the long peptide chains. The fact that the natural protein spread very much better than the denatured indicates that the internal structure of the protein molecule in solution is strengthened, not weakened, by denaturation.

The effect of irradiation seems to be slightly different from that of heat. The amount of irradiation given to the protein solutions (pH 4.4) in the quartz cell before spreading was sufficient to cause complete precipitation of solutions at the isoelectric point, yet, though the spreading was diminished, it was not entirely destroyed. It is interesting that irradiation of the spread films, i.e., of the completely uncoiled form of the molecules, causes some degree of coiling, evident through the collapse of the film. This may be because it is mainly the free COO^- and NH_3^+ groups which anchor the spread film to the surface and keep it spread. Further work has to be done for a complete elucidation of this effect.

The slight difference between the spreading of serum and egg albumin may be due to the greater number of water-attractive groups of serum albumin. Serum albumin, spreading to a 15 per cent larger area per gram than egg albumin, has about one hundred and three carboxyl and one hundred and twelve amino groups per molecule; egg albumin, thirty and thirty-six respectively (Pauli and Valko (13)). Also a comparatively small internal cohesion of the serum albumin molecule, as concluded from colloid chemical experience by Pauli (12, 13), might account for the greater ease of its unfolding.

SUMMARY

Egg albumin and serum albumin have been spread on aqueous buffer solutions at the isoelectric point and at pH 4.4. Serum albumin spreads to an about 15 per cent greater area, per gram, than egg albumin. The spreading is completely destroyed by previous denaturation of the solutions by heat, and partially destroyed by denaturation by irradiation; a fully spread film can be caused to collapse to a considerable extent by irradiation.

The bearing of these experiments on theories of denaturation is discussed. It is probable that denaturation both diminishes the attraction of the protein for water through the combination, within the molecule, of carboxyl and amino groups previously free; also the same combination probably tightens the internal structure of the protein molecule, making it more difficult to uncoil on the surface.

My heartiest thanks are due to Professor F. G. Donnan, F. R. S., for his generous hospitality and his interest and to Dr. N. K. Adam, F. R. S., for his very helpful criticism and advice.

REFERENCES

- (1) ADAM, N. K.: *The Physics and Chemistry of Surfaces*. Oxford University Press, London (1930).
- (2) ADAM AND JESSOP: *Proc. Roy. Soc. London* **110A**, 423 (1926).
- (3) ASTBURY, W. T., AND LOMAX, R.: *J. Chem. Soc.* **1935**, 846.
- (4) DU NOUY: *Surface Equilibria of Biological and Organic Colloids*. The Chemical Catalog Co., Inc., New York (1926).
- (5) FOSSBINDER, R. J., AND LESSIG, A.: *J. Franklin Inst.* **215**, 579 (1933).
- (6) GORTER, E., AND GRENDL, F.: *Proc. Acad. Sci. Amsterdam* **29**, 371 (1926).
- (7) GORTER, E., AND PHILIPPI, G. TH.: *Proc. Acad. Sci. Amsterdam* **37**, No. 10 (1934).
- (8) GORTER, E., VAN ORMONDT, J., AND DOM, F. J. P.: *Proc. Acad. Sci. Amsterdam* **35**, No. 6 (1932).
- (9) HAUROWITZ, F.: *Kolloid-Z.* **71**, 199 (1935).
- (10) HUGHES, A. H.: *Trans. Faraday Soc.* **29**, 211 (1933).
- (11) HUGHES, A. H., AND RIDEAL, E. K.: *Proc. Roy. Soc. London* **137A**, 62 (1932).
- (12) PAULI, W., AND FENT, P.: *Kolloid-Z.* **67**, 228 (1934).
- (13) PAULI, W., AND VALKO, E.: *Die Kolloidchemie der Eiweisskörper*. Theodor Steinkopff, Dresden (1933).
- (14) PAULI, W., AND WEISS, R.: *Biochem. Z.* **233**, 381 (1931).
- (15) RAMSDEN, W.: *Z. physik. Chem.* **47**, 336 (1904).
- (16) SCHULMAN, J. H., AND RIDEAL, E. K.: *Biochem. J.* **27**, 1581 (1933).
- (17) SVEDBERG, THE, AND NICHOLS, J. B.: *J. Am. Chem. Soc.* **48**, 3081 (1926); **49**, 2920 (1927).
- (18) SVEDBERG, THE, AND SJOEGREN, B.: *J. Am. Chem. Soc.* **50**, 3318 (1928).
- (19) ZOCHER AND STIEBEL: *Z. physik. Chem.* **147A**, 401 (1930).

THE FORMATION OF LIESEGANG RINGS IN THE PRESENCE OF PRECIPITATES

BINAYENDRA NATH SEN

Chemical Laboratory, Presidency College, Calcutta, India

Received September 18, 1935

Much work has been done on the formation of periodic bands of precipitates of different substances in the presence of gels. It has been almost generally believed that gels are almost essential for such types of periodic precipitation, though the number of instances in which the formation of Liesegang rings is discernible even in the absence of gels has increased (4, 5, 6, 8) comparatively recently. It is the object of the present paper to report the formation of such periodic bands of precipitates, not in a gel but in the presence of certain other precipitates where the specific characteristics of gel-structure are absent and where the probability of the co-existence of sol and the precipitate of the same substance (1, 2, 3, 4), if not absent, would appear to play no prominent function. It is very difficult to explain the occurrence of such bands in the presence of these insoluble substances unless adequate experimental data are available, but it may be suggested that selective adsorption of some of the ionic species in the system by these precipitates may in all probability play a very important rôle in such a phenomenon.

EXPERIMENTAL

The calcium sulfate and the barium sulfate were powdered to a very fine state of subdivision. Into thoroughly cleaned test tubes known volumes of a solution of ferric chloride of known concentration were introduced and then 10 g. of the extremely fine powder of each of the precipitates was allowed to drop in. A further known volume of the solution of ferric chloride was next introduced into each of the test tubes. The exact volume of the solution to be added was found by trial, and such a volume was selected that when the 10 g. of powdered precipitate was placed in the solution, the mass of the precipitate would completely absorb the solution on standing. The precipitates in contact with the solution were allowed to stand for eight hours. The contents of the tubes were next centrifuged and kept overnight. It was then found that the mass of precipitate, after absorbing the solution completely, appeared to present some resemblance to a thickly set uniform gel of agar. It was, however, not transparent.

A known volume of the solution of potassium ferrocyanide of known concentration was then carefully added to the precipitate without causing any disturbance of the solid particles. The test tubes with their contents were then allowed to stand for days, and the changes were noted each day until the Prussian blue precipitate had reached the bottom of each tube.

As it has been brought out by the experiments of Lloyd and Moravek (7) that carrying out the reaction in a small space exerts a marked favorable influence on the formation of Liesegang rings, experiments were also performed in much the same way in tubes of narrow bore, having internal diameters of 0.5 and 0.25 cm. However, these experiments yielded no positive results.

It may be mentioned that 8 cc. of the ferric chloride solution was necessary for 10 g. of the calcium sulfate precipitate for complete absorption by the said precipitate; 4 cc. of the ferric chloride was added before and another 4 cc. after the introduction of the calcium sulfate into the test tube. In the case of barium sulfate, however, 6 cc. of the solution was necessary, of which 3 cc. was added before and 3 cc. after the introduction of the



FIG. 1. Liesegang rings obtained by using 10 g. of calcium sulfate, 8 cc. of 0.385 *N* ferric chloride, and 6 cc. of 1.15 *N* potassium ferrocyanide

sulfate precipitate. The purpose in introducing some of the solution before the introduction of the precipitate was to minimize the possibility of the air bubbles being kept enclosed in the bodies of the solid precipitates. Care was always taken to ensure that no air bubbles could have a chance to remain thus enclosed.

RESULTS WITH CALCIUM SULFATE

The number of rings formed increased with the dilution of the ferric chloride solution, and the distance between the rings decreased as the concentration of the ferric chloride was increased. The concentration of the potassium ferrocyanide appeared to have no favorable influence on the formation of the rings (1.15 *N* solution was used in the experiments).

The first ring appeared after about forty hours; then another ring came in the course of a day.

The distance between these two rings was quite considerable. The thickness of the first ring was, however, greater than that of the second. The distance of the first ring from the surface of separation of the solid and the

solution was about one-fourth the distance between the first and the second rings at favorable concentrations of ferric chloride.

After the appearance of the second ring the blue color proceeded downward, uniform in tint but weaker in shade. The progress continued for several days and then ceased. This position was maintained for about three days. At the end of that time there appeared a distinctly blue ring, much deeper in shade than the blue color which had just ceased moving, and uniformly thick, its lower edge coinciding with the edge of the blue tint which had ceased to move downward. The blue tint above the ring became lighter and lighter in shade; after a day a ring appeared above it making the intervening space colorless. Another ring appeared again above this second ring in the course of a day, and the intervening space again lost its color. In this way, a ring appeared every day until there were five successive rings. After the formation of the fifth ring in the series, no fresh rings appeared. The rings were stable and distinct for about a week, after which they began losing their distinctness. As soon as the rings began losing their distinctness, the blue color started travelling down from the lowermost ring, slowly and gradually, until it came to the bottom. This occurred in the course of another week. Even when the blue color had reached the bottom, the rings previously formed, though indistinct, were yet discernible and about a month more was required for them to lose their identity completely. It may be mentioned that the distance between the rings in the above series increased only slightly in the order of the sequence of appearance of the rings. It is also of interest to note that no periodicity in the precipitation was observed in the region below the above series of rings, through which the blue tint ultimately travelled down.

At very high concentrations of ferric chloride (above 1.5 *N*), two semicircular highly colored patches appeared just below the surface of separation of the liquid and the solid. No ring, however, was found to appear, even after keeping the system for about a week, but at the end of the week several periodic bands were observed in these highly colored spots in the form of arcs of circles.

At moderately high concentrations of ferric chloride (0.75–1.5 *N*), however, these two deeply colored patches also appeared but with increased areas, and a highly colored ring appeared 8 mm. below these two areas. In the course of about three days another ring appeared just above; this was succeeded in its upper region by three fully developed rings and three partly developed rings at equal distances apart, the last partly developed ring touching the lower borders of these spots. In the meantime, there appeared several periodic bands in the form of arcs of circles in each of the highly colored semicircular patches. The most favorable concentrations of ferric chloride for ring formation are in the range 0.3–0.6 *N*.

RESULTS WITH BARIUM SULFATE

In the case of barium sulfate, however, it was somewhat difficult to obtain the periodic bands. It appeared to be difficult as well to study the probability of the formation of the rings with reference to the concentration of the ferric chloride, the concentration of the potassium ferrocyanide having apparently no influence on the ring formation. In most concentrations no rings were obtained; if formed at all at some concentration, they were comparatively indistinct. The range of concentrations in which the ring formation was favored was also very narrow (0.15–0.25 *N*). It was only in this small range of concentration of the ferric chloride that comparatively distinct rings, though lighter in shade than those obtained in the body of the calcium sulfate precipitate, were obtained. In 0.2 *N* ferric chloride the most distinct rings were obtained, and three rings were discernible. The distances between the rings were approximately equal, but the thickness of the first ring was greater than that of the second and that of the second was greater than that of the third. The thickness of the rings was, however, considerably greater than that of those obtained in the body of calcium sulfate; the rate of travel of the blue color through the precipitate was also comparatively rapid.

SUMMARY

The formation of Liesegang rings of Prussian blue in the bodies of calcium sulfate and barium sulfate, moistened with ferric chloride solution, has been recorded.

The influence of the concentration of the ferric chloride on the characteristics of the rings has been studied.

My best thanks are due to Dr. P. Neogi for giving me facilities for carrying on this piece of work.

REFERENCES

- (1) DEAR AND CHATTERJEE: *J. Phys. Chem.* **28**, 41 (1924).
- (2) DEAR AND CHATTERJEE: *Kolloid-Z.* **37**, 3, 89 (1925).
- (3) DEAR AND CHATTERJEE: *Z. anorg. Chem.* **159**, 129, 186 (1926).
- (4) DEAR AND MITRA: *Nature* **761**, May 21, 1932.
- (5) FISCHER AND SCHMIDT: *Roczniki Chem.* **6**, 404 (1926).
- (6) HEDGES: *J. Chem. Soc.* **1929**, 2779.
- (7) LLOYD AND MORAVEK: *J. Phys. Chem.* **36**, 1514 (1931).
- (8) MORSE: *J. Phys. Chem.* **34**, 1554 (1930).

NOTE ON THERMODYNAMIC EQUILIBRIUM IN THE GRAVITATIONAL FIELD

F. O. KOENIG

Department of Chemistry, Stanford University, California

Received September 18, 1955

I. THE FUNDAMENTAL GIBBSIAN EQUATIONS FOR THE CHARACTERISTIC FUNCTIONS OF A SUBPHASE

In his excellent treatise, E. A. Guggenheim (1) has recently given an exact (non-relativistic) account of thermodynamic equilibrium in gravitational fields, starting from differential equations of Gibbsian type for the characteristic functions of an infinitely thin homogeneous layer of matter of given gravitational potential. Thus for the energy, E^α , of such a layer, α , he writes

$$dE^\alpha = T^\alpha dS^\alpha - P^\alpha dV^\alpha + \sum_i (\mu_i^\alpha + \bar{M}_i \varphi^\alpha) dn_i^\alpha \quad (1)$$

where T^α , S^α , P^α , V^α , and φ^α denote respectively temperature, entropy, pressure, volume, and gravitational potential of the layer, n_i^α the number of moles of the i^{th} component in the layer, \bar{M}_i the molecular weight of the i^{th} component, and μ_i^α a function which is assumed to be completely determined by P^α , T^α , n_i^α .

It seems worth pointing out, for reasons stated below, that equation 1 can be generalized so as to take account of the fact that the energy of the layer in question can be varied without absorption of heat ($T^\alpha dS^\alpha$), performance of volume work ($-P^\alpha dV^\alpha$), or changes of composition ($(\mu_i^\alpha + \bar{M}_i \varphi^\alpha) dn_i^\alpha$), merely by a change of gravitational potential φ^α , as for instance through a shift of level in the earth's field. The contribution to E^α of an infinitesimal change in φ^α at constant S^α , V^α , n_i^α is evidently $M^\alpha d\varphi^\alpha$ where M^α is the mass of the layer.

Equation 1 is accordingly replaced by

$$dE = TdS - PdV + Md\varphi + \sum_i \tau_i dn_i \quad (2.1)$$

where for simplicity the superscript α is omitted and the sum $\mu_i + \bar{M}_i \varphi$ denoted by τ_i . Of the variables E , S , V , n_i , φ all but one are independent, so that if the number of components is k , the number of independent differentials in equation 2.1 is $k + 3$. The corresponding equations for

the other characteristic functions, i.e., the heat content H , the Gibbs free energy F , and the Helmholtz free energy A , are of course

$$dH = VdP + TdS + Md\varphi + \sum_i \tau_i dn_i \quad (2.2)$$

$$dF = -SdT + VdP + Md\varphi + \sum_i \tau_i dn_i \quad (2.3)$$

$$dA = -PdV - SdT + Md\varphi + \sum_i \tau_i dn_i \quad (2.4)$$

For convenience the thin layer to which these equations apply may be called a "subphase."

The new equations (2) are of interest because (i) they further illustrate the point clearly made by Guggenheim (ref. 1, p. 154) that "the gravitational potential difference φ^α between two [sub-]phases, in contrast to the electric potential difference ψ^α is thermodynamically determinate, owing to the fact that its value is independent of the presence and nature of the phase there;" (ii) they show that the statement (ref. 1, p. 154) that "in all thermodynamic formulae the quantity φ^α occurs only in combinations of the form $(\mu_i^\alpha + M_i\varphi^\alpha)$ " is generally true *only* for changes at constant φ^α ; (iii) they are of the same form as the general thermodynamic equations for external electric and magnetic fields (2) and thus serve to emphasize certain important analogies. Equations 2 furthermore yield deductions of the laws of hydrostatic equilibrium and of sedimentation equilibrium which to the author seem more concise than previous ones and are accordingly given below. These deductions fall naturally into the stages indicated by the titles of the following paragraphs.

II. THERMAL AND CHEMICAL EQUILIBRIUM BETWEEN SUBPHASES

The general criteria for thermodynamic equilibrium in conjunction with the equations 2 lead in the usual manner to the familiar conditions

$$T^\alpha = T^\beta \quad (3)$$

$$\tau_i^\alpha = \tau_i^\beta \quad (4)$$

for thermal and chemical equilibrium, respectively, between any two subphases α and β .

III. THE GIBBS-DUHEM EQUATION FOR A SUBPHASE

The energy of a subphase like that of a bulk phase (in the absence of gravity) is clearly homogeneous of the first order in the capacity factors S , V , n_i . By Euler's theorem equation 2.1 therefore yields

$$E = TS - PV + \sum_i \tau_i n_i \quad (5)$$

which, on differentiation and comparison with equation 2.1 in the usual manner, gives

$$SdT - VdP - Md\varphi + \sum n_i d\tau_i = 0 \quad (6)$$

the analogue of the Gibbs-Duhem equation for a bulk phase. For the treatment of hydrostatic and sedimentation equilibrium it is convenient to write equation 6 in the form

$$dP = sdT - \rho d\varphi + \sum_i c_i d\tau_i \quad (7)$$

where s is the entropy per unit volume, c_i the volume concentration of the i^{th} component, and ρ the density of the subphase. Of the $k + 3$ intensive variables T, P, φ, τ_i in equations 6 and 7, any $k + 2$ are independent.

IV. HYDROSTATIC EQUILIBRIUM

If T, φ, τ_i are taken as the independent variables, it follows from equation 7 that for any subphase

$$\left(\frac{\partial P}{\partial \varphi} \right)_{\tau, \tau_i} = -\rho \quad (8)$$

Now by equations 3 and 4 all the (infinitely numerous) subphases of a fluid in thermal and chemical equilibrium have the same values of T and of the τ_i . But since any two adjacent subphases whatever differ infinitesimally in φ , it follows from equation 8 that any fluid in thermal and chemical equilibrium in a gravitational field is also in hydrostatic equilibrium, i.e., that

$$^*dP = -\rho d\varphi \quad (9)$$

where the operator d refers to the difference between two adjacent subphases. Any equation such as equation 9, in which d has this significance, is conveniently prefixed by an asterisk, to distinguish it from equations such as 1, 2, 6, 7 in which d refers to an infinitesimal change within a single subphase.

V. ACTIVITY COEFFICIENTS IN A SUBPHASE

For compactness in the expression for sedimentation equilibrium to be derived below it is expedient to introduce activity coefficients defined in a manner analogous to that for a bulk phase (ref. 1, p. 115), namely

$$\mu_i \equiv \mu_i^0(T, P) + RT \log N_i f_i \quad (10)$$

where μ_i^0 is a function only of T and P , N_i is the mole fraction of the i^{th} component in the subphase, and f_i is its activity coefficient, that is, a

function of T, P, n_i so chosen as to be unity at infinite dilution. This definition evidently implies that μ_i is completely determined independently of φ by T, P, n_i alone, a fact readily proved from the equations 2, which herein reveal a decided advantage over the equations of type 1. From equation 2.3 it follows that

$$\left(\frac{\partial \tau_i}{\partial \varphi}\right)_{T, P, n_i} = \left(\frac{\partial M}{\partial n_i}\right)_{T, P, n_i', \varphi} \quad (11)$$

where the subscript n_i' indicates the constancy of all the n_i except a particular one with respect to which the differentiation is carried out. The introduction of the relations

$$\tau_i \equiv \mu_i + \bar{M}_i \varphi \quad (12)$$

$$M = \sum_i n_i \bar{M}_i \quad (13)$$

into equation 11 gives

$$\left(\frac{\partial \mu_i}{\partial \varphi}\right)_{T, P, n_i} = 0 \quad (14)$$

$$\mu_i = \mu_i(T, P, n_i) \quad (15)$$

VI. PARTIAL MOLAR VOLUMES AND PARTIAL MOLAR ENTROPIES IN A SUBPHASE

Besides the activity coefficients f_i it is expedient to introduce the partial molar volumes \bar{V}_i and the partial molar entropies \bar{S}_i . That these quantities as well as V and S themselves are functions of T, P, n_i alone follows from equation 2.3 by proofs similar to the one given above for μ_i . Particularly useful for compact derivation of the law of sedimentation equilibrium are two equations readily deduced from equations 2.3, 12, and 10, namely

$$\left(\frac{\partial \mu_i^0}{\partial P}\right)_T = \bar{V}_i^0 \quad (16)$$

$$\left(\frac{\partial \mu_i^0}{\partial T}\right)_P = -\bar{S}_i^0 \quad (17)$$

in which \bar{V}_i^0 and \bar{S}_i^0 denote the values of \bar{V}_i and \bar{S}_i at infinite dilution.

VII. SEDIMENTATION EQUILIBRIUM

From equation 12 it follows that for any component of a subphase, say the j^{th} ,

$$d\mu_j + \bar{M}_j d\varphi - d\tau_j = 0 \quad (18)$$

Differentiation of equation 10 and substitution of the result into equation 18 gives

$$\left(\frac{\partial \mu_j^0}{\partial T}\right)_P dT + \left(\frac{\partial \mu_j^0}{\partial P}\right)_T dP + RT d \log N_j f_j + R \log N_j f_j dT + \bar{M}_j d\varphi - d\tau_j = 0 \quad (19)$$

which, on introduction of equations 16 and 17 and elimination of dP by means of equation 7, becomes

$$RT d \log N_j f_j - (\rho \bar{V}_j^0 - \bar{M}_j) d\varphi + (s \bar{V}_j^0 - \bar{S}_j^0 + R \log N_j f_j) dT + \bar{V}_j^0 \sum_i c_i d\tau_i - d\tau_j = 0 \quad (20)$$

If T, φ, τ_i are taken to be the independent variables it follows that in any subphase

$$RT \left(\frac{\partial \log N_j f_j}{\partial \varphi} \right)_{T, \tau_i} = \rho \bar{V}_j^0 - \bar{M}_j \quad (21)$$

for each component. This equation in conjunction with equations 3 and 4 shows that in any *solution in thermal and chemical equilibrium in a gravitational field*

$$*RT d \log N_j f_j = (\rho \bar{V}_j^0 - \bar{M}_j) d\varphi \quad (22)$$

for each component. Equation 22 is the exact law of sedimentation equilibrium in a form more compact than any hitherto given. It is readily shown to be identical with the expression given by Guggenheim (ref. 1, p. 157).

The integration of the sedimentation equation, neglecting compressibility, has been carried out by Guggenheim (ref. 1, pp. 157-8) for the binary ideal solution of any concentration and for the "extremely dilute" ideal solution of any number of components. The result for a third simple case of physical interest, that of the "extremely dilute" non-ideal solution of any number of components, seems worth giving; it is

$$\log \frac{N_j^\alpha f_j^\alpha}{N_j^\beta f_j^\beta} = \log \frac{c_j^\alpha f_j^\alpha}{c_j^\beta f_j^\beta} = (\rho_0 \bar{V}_j^0 - \bar{M}_j) \frac{\varphi^\alpha - \varphi^\beta}{RT} \quad (23)$$

where ρ_0 is the density of the pure solvent.

VIII. SUMMARY

The fundamental equations for the thermodynamics of the gravitational field are written in a form more general than hitherto by the inclusion of

the gravitational potential ϕ as an independent variable. The theoretical interest of the resulting new equations is briefly pointed out, and their practical usefulness shown by deducing from them the known laws of hydrostatic equilibrium and sedimentation equilibrium. The latter law is expressed in a new and compact form involving the activity coefficient.

REFERENCES

- (1) GUGGENHEIM, E. A.: *Modern Thermodynamics by the Methods of Willard Gibbs*, pp. 153-9. Methuen and Co., London (1933).
- (2) KOENIG, F. O.: Paper read before the Division of Physical and Inorganic Chemistry of the American Chemical Society, San Francisco, August, 1935.

A COMPARATIVE METHOD FOR MEASURING AQUEOUS VAPOR AND DISSOCIATION PRESSURES, WITH SOME OF ITS APPLICATIONS¹

E. M. COLLINS AND ALAN W. C. MENZIES

Frick Chemical Laboratory, Princeton University, Princeton, New Jersey

Received August 31, 1935

The method here described is a comparative one because the aqueous pressure over an aqueous sulfuric acid solution, whose concentration can later be found, becomes equal at the same temperature to the aqueous pressure of the system under investigation. Since the variation of aqueous pressure with temperature of the two systems thus under comparison is, fortunately, very similar, refined temperature control is not a necessity. Measurements may therefore be made with ease up to temperatures well over 100°C., at which close control of temperature over lengthy periods has proved difficult to most workers. It is in part due to this difficulty that records of measurements of dissociation pressures of salt hydrate systems are scanty as well as notoriously discordant for temperatures much above room temperature, and we believe that this situation can be remedied by use of the method here described. It is essential to realize, however, that in measurements of dissociation pressures, there enters at the lower temperatures another little understood source of error which must be avoided, especially in dealing with systems of lower hydrates which of necessity exhibit very large surface areas when prepared by efflorescence from higher hydrates. The errors in question have been attributed to adsorbed water (23) and are here further discussed in the light of experimental results which we believe are little vitiated by the better recognized sources of error.

We shall show below the application of our procedure to the measurement of the aqueous pressures of saturated solutions and to the dissociation pressures of salt hydrate systems.

COMMENTS UPON CERTAIN OTHER METHODS

The first three methods mentioned below, because absolute rather than relative or comparative, require accurate temperature control, which is the more difficult the higher the temperature.

¹ From a thesis presented by Edward M. Collins to the Faculty of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, January, 1933.

(1). The Bremer-Frowein tensimeter and its modifications (12, 34, 22, 6) are difficult to free from permanent gases, which may be but slowly released from solid phases (22).

(2). The isoteniscope (37) has the advantage that it can be freed from permanent gases by repeated trial until constant results are obtained, and thus it has been used successfully in many cases in which equilibrium is reached quickly (10).

(3). The gas current saturation method, although often successfully employed (22, 1, 2, 3, 35, 29), is cumbersome, requires much material, and is difficult in cases of slow equilibrium (1). It is not open to the objection suggested by Partington (28, 22).

(4). Those indirect methods which depend on equilibration with water through the liquid phase of salt hydrate systems in contact with this water dissolved in such liquids as ether (19), ethyl alcohol (11), isoamyl alcohol (27), nitrobenzene (32, 36), benzene or chloroform (23) are not as rapid as had been hoped, demand insolubility of the salts in the experimental liquid, and are obviously less suitable for higher temperatures.

(5). Lastly may be mentioned that indirect method which depends upon ascertaining by trial the concentration of an excess of aqueous sulfuric acid from or to which the system under investigation neither gains nor loses water through the vapor phase (25, 43, 21, 44). The method is commonly operated in the presence of air and is time-consuming, while the equilibrium concentration of acid cannot safely be judged by the rate of approach from either side; but refined temperature control has indeed proved unnecessary (43, 21).

OUTLINE OF METHOD HERE ADOPTED

The principle of our method is the same as of the method last mentioned, namely equilibration through the vapor phase with aqueous sulfuric acid. We allow the acid, however, automatically to alter its own concentration until its aqueous pressure matches that of the material under investigation, which, in the present work, is either a salt hydrate pair or a saturated solution. The acid, contained in an elongated weighing tube, which can be stoppered by the device of Richards (30), is stirred by mechanical rocking through about 20° of arc. In order to lessen the weight of water to be transferred in the process of equilibration, we use only about 0.2 g. of acid of known concentration, accurately weighed out. We furnish an abundant supply of the material that must govern the final pressure by using quantities of 10 to 20 g. We accelerate the transfer of water by removal of other gases. This is simply achieved by precooling, exhausting and sealing off an ordinary 2×15 cm. test tube which contains both the material and the acid weighing tube. Since our apparatus is sealed, we are no longer limited to pressures below one atmosphere. Because the

essential portion of the apparatus is thus contained within a relatively small tube, we are able to run four determinations simultaneously in eight tubes placed in one cradle, each substance utilizing two test tubes, one with acid more, the other with acid less concentrated than the expected equilibrium concentration. Uniformity of temperature throughout each tube is ensured, especially above $50^{\circ}\text{C}.$, by inclosing each in a short length of iron or copper pipe with capped ends. The desired temperature is maintained with sufficient steadiness in an ordinary Freas constant-temperature oven of one cubic foot capacity, the air of which is stirred by a fan driven by the same motor that rocks the cradle. In the normal case, we run the experiments overnight for convenience, and normally find in the morning that equilibrium has been reached from both sides. The minimum time necessary varies with circumstances from a couple of hours or less in simple cases to many days in difficult cases.

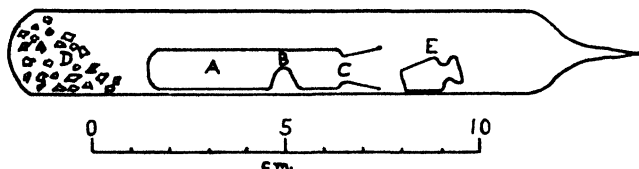


FIG. 1. Weighing tube within sealed test tube

EXPERIMENTAL DETAILS

Figure 1 shows the acid-containing weighing tube ABC confined within the same sealed test tube as the substance D. Tube ABC may be kept in position by means, for example, of a tuft of steel wool wedged between it and the test tube. The acid itself is present only in portion A which is separated from the mouth of the tube by the barrier B, formed by indenting the Pyrex glass while heated at this point. The ground glass stopper E is shown ready in position to be dropped home on erecting the tube. This process of stoppering is carried out at the temperature of the oven. After stoppering the acid tube, air is immediately admitted by breaking the sealed tip of the containing test tube, the apparatus is allowed to cool and finally cut open to release the acid tube for weighing. The final concentration of the acid is found by comparison of its final weight with its original weight and known concentration. A small correction due to the weight of the water vapor stoppered within the weighing tube is applied when necessary at higher temperatures. The dimensions of the apparatus are made obvious by the scale of centimeters on the diagram. Prior to evacuation, the test tube with its contents is cooled in a freezing mixture to minimize loss of water during evacuation, which may be carried by a

Hyvac pump below 0.2 mm. of mercury as measured by a simple MacLeod gauge.

When the substance D was a pair of salt hydrates, precaution was taken to effloresce the higher hydrate about halfway towards the composition of the lower hydrate so as to secure as large a number of active growth spots as possible. This precaution is well worth while, since Carpenter and Jette (6), who only "slightly effloresced" their higher hydrates, required much longer to reach equilibrium values than did Menzies (22) under similar conditions. The grain size of the hydrates used was not uniform but approximated 15 mesh.

When the vapor pressure of saturated solutions was desired, the portion D contained initially the highest hydrate moistened with its saturated solution. The attainment of identical final acid concentrations starting from stronger and weaker acid solutions respectively in a pair of tubes containing the same substance was in itself sufficient evidence that equilibrium between solid, solution, and vapor had been established.

Experiment showed that the rate of loss or gain of water from or by a salt hydrate pair was always, under our conditions, a slower process overall than the rate of transfer of water to or from the stirred acid. The active surface of salts used, therefore, governed the speed of the process of equilibration. Adequate stirring of the acid was secured by mechanically rocking the tubes about fifteen times per minute by means of an eccentric device upon a reducing gear.

CONTROL OF TEMPERATURE

In respect to the smallness of angle with which the temperature-pressure curves of other water vapor-yielding systems cut the curve of an aqueous sulfuric acid solution there are, naturally, differences according to the nature of these systems. But the angle is uniformly a small angle, and thus change of temperature influences the relative humidity of the two in a much smaller degree than it does their absolute aqueous pressures. Illustrating this in the case of dissociating cupric sulfate pentahydrate, the temperature error, at 25° and 50°C., sufficient to produce an error in the dissociation pressure measurement of 1 per cent is 0.2° and 0.2°C., respectively, for any absolute measurement and 2° and 1°C., respectively, for the present method. In general, for the systems studied by us at 50°C., the average temperature divergence to produce an error in pressure not greater than 1 per cent is 1° to 2°C.

By using a simple mechanical device to open momentarily the heating-current contact points of the automatic temperature regulator of our oven every half-minute, thus minimizing overshooting of temperature caused by adhering of these points, we were able to secure constancy of temperature at all temperatures used to within 0.5°C. The absolute measurement

of temperature to 0.1°C. was made possible by comparisons from time to time with certificated standard thermometers after redetermination of their zero points. It will be understood that temperature precision is here of much less moment than it was in establishing the water pressures over aqueous sulfuric acid (8).

CHOICE OF SULFURIC ACID AS COMPARISON LIQUID

We contemplated and rejected the use of other substances. We learned (41) that sulfuric acid solutions not over 80 per cent lose by vaporization no sulfur below 220°C., while 89 per cent acid has a partial pressure ascribed to H_2SO_4 of only 0.5 mm. at 290°C. (40). We proved by gravimetric and volumetric methods that no measurable amount of either sulfate or acid hydrogen was lost from our weighing tubes at our highest experimental temperatures, either by evaporation or by action on the Pyrex glass. Furthermore, the Pyrex weighing tubes used for the acid remained constant in weight throughout.

Because we found that the values in the literature for the vapor pressures of aqueous sulfuric acid solutions at various temperatures were not concordant, these values were redetermined and have been reported elsewhere, as has also the preparation of the sulfuric acid solutions used in the present work (8).

PURITY OF SALTS USED

These salts were prepared by recrystallization of reagents of the highest purity (26). None contained more than 0.002 per cent of heavy metals as impurities. The possibly large influence of impurities upon the dissociation pressures of salt hydrates has seldom been recognized, and it is often forgotten; for example, 1 per cent of manganese sulfate in the mixed crystal lowers the dissociation pressure of cupric sulfate pentahydrate by 8.6 per cent at 20°C. (14). Our cupric sulfate was found to contain not more than 0.001 per cent of nitrates, chlorides, alkalis, or alkaline earths. The barium chloride and barium bromide contained not more than 0.02 per cent of strontium and calcium, and less than 0.1 per cent of the alkalis. The bromide contained less than 0.002 per cent of chloride. The strontium chloride and bromide were free from barium and calcium to the extent of 0.01 per cent, and from the alkalis to the extent of 0.05 per cent. The bromide contained less than 0.002 per cent chloride. The barium and strontium bromides were entirely free from bromate. The calcium chloride contained not over 0.002 per cent of barium and strontium, and less than 0.05 per cent of the alkalis.

ANOMALOUS RESULTS AND THEIR INTERPRETATION

In studies of the dissociation pressures of salt hydrates, it has been too often tacitly assumed that we are dealing from the start with nothing but

two crystalline phases and one vapor phase. That this assumption is apparently allowable in certain cases was shown, for example, by Bolte (4), and in these cases he obtained in a reasonable time at constant temperature a pressure that was constant for all compositions of material intermediate in water content between those of the nearest two stoichiometrical hydrates. The two crystalline phases are presumably active in their control of aqueous pressure only at those points on a surface where they are in contact (18, 9),—the active spots. If merely vapor were present above such spots, all might be well from the phase rule standpoint, and early measurements yield the same pressure values as later ones. But if the surface is masked by a layer of non-vaporous water, the crystalline picture is blurred, and the simple phase rule prediction may be temporarily or more permanently unrealized according to the persistence of the layer. This layer has influence only at the active spots, but the mobility of its members may be much less than that of a two-dimensional gas, if one may use this method of expressing the energy of its binding. For this reason its influence upon the apparent dissociation pressure may be long-enduring. Whether its mode of attachment is physical or chemical is a purely academic question, as is the nature of attachment of a common ion from solution adsorbed preferentially upon a crystalline precipitate. One may recall in this connection the curious fact established by Menzies and Potter (24) in 1912 that dehydration of a hydrate may be more rapid and more thorough in the presence of increased pressures of water vapor. This has been confirmed recently in another instance by Topley and Smith (42).

Such considerations suggest an explanation of the difficulties and anomalous results encountered in the measurements of dissociation pressures, by Bolte (4, 5) for carnallite and for kainite; by Schumb (35), by Baxter and Cooper (1), and by Partington (28) for barium chloride dihydrate; by Carpenter and Jette (17) for nickel sulfate hexahydrate; and in many earlier cases. They may explain the high results of the last named workers for cupric sulfate trihydrate at 25° and 35°C., and likewise many other high results in the lower ranges of temperature to be found in the literature, as well as unnumbered disappointing results which, as suggested by Hackspill and Kieffer (13), have never been published because equivocal and discouraging to those who found them.

The question has already been discussed elsewhere by Menzies and Hitchcock (23), and we shall here briefly set down some of our conclusions substantiated by the present work. We find: (1) that the difficulty becomes less apparent the higher the temperature, as might be expected; (2) that material which has, for purposes of measurement, previously been in contact with a higher pressure of water vapor at a higher temperature is prone to yield too high pressure values for lower temperature measurements

which immediately succeed them; (3) that, in certain cases, a genuine equilibrium pressure appears to present itself in experiments of customary duration, which falls in value only slowly with time. For example, samples of cupric sulfate trihydrate with the monohydrate, previously used at 100°C., reached "normal" pressure values only after five days in a subsequent experiment at 50°C., falling progressively in pressure at 50°C. from over 40 to 30.5 mm.; (4) that, with different hydrate pairs, the abnormality is the greater the lower the dissociation pressure for the same temperature; (5) that, if the material for investigation must be prepared by efflorescence, the anomaly is best avoided by preventing undue access of water vapor to the material prior to measurements.

TABLE 1
Dissociation pressures for the system $\text{SrCl}_2 \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{SrCl}_2 \cdot \text{H}_2\text{O} + \text{H}_2\text{O}$

<i>t</i>	INITIAL AND FINAL CON- CENTRATION OF H_2SO_4	RELATIVE VAPOR PRESSURE	<i>P</i>
°C.	<i>per cent</i>		<i>mm.</i>
25	80 → 65.8	9 02	2.14
	65 → 66.3	8 45	2 01
50	66 → 64 0	13.2	12 2
	54 → 64 0	13 2	12 2
75	63 → 60 6	20 7	59.7
	55 → 60 7	20 5	59 3
90	59 → 58 4	25 9	136 1
	42 → 58 1	26 6	139.6
100	65 → 56 3	31 1	236.0
	45 → 56 2	31.3	237.7
110	61 → 54 4	36 1	388.2
	52 → 54.2	36 6	393.6
125	52 → 50 3	46 0	803.5
	43 → 50 5	45 6	794.3
130	50 → 49.4	48.2	975.0
	45 → 48.8	49.2	997 7

Hydrates which (in the presence of the next lower hydrate) have, if improperly treated, shown this anomaly in the present work are the following: cupric sulfate trihydrate and the dihydrates of barium chloride, barium bromide, and strontium chloride.

It is hoped to correlate these experimental findings in the light of better knowledge of crystal structure.

DETAILS OF ONE SERIES OF MEASUREMENTS

In table 1 we give details of our measurements upon a single system, namely $\text{SrCl}_2 \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{SrCl}_2 \cdot \text{H}_2\text{O} + \text{H}_2\text{O}$. In the second column are stated the initial and final concentrations of sulfuric acid in the two experi-

TABLE 2a

Aqueous vapor and dissociation pressures of cupric sulfate hydrate systems

<i>t</i> IN °C.	<i>P</i> CALCD.	<i>P</i> OBSD.	<i>P</i> (FOUND BY OTHERS)	<i>t</i> IN °C.	<i>P</i> CALCD.	<i>P</i> OBSD.	<i>P</i> (FOUND BY OTHERS)
CuSO ₄ , saturated solution							
Solid phase: CuSO ₄ ·5H ₂ O				95	550.8	550.8 552.1	
25	23.1	23.0 23.1	23.16 (38)	95.88	568.7	(transition temperature)	tempera-
30	30.9		30.93 (38)	Solid phase: CuSO ₄ ·3H ₂ O			
35	40.7			100	656.1	656.1 659.2	659.7 (38)
40	53.3		53.39 (38)	105	775.0		
45	68.9			110	911.8	909.9 909.9	
50	88.1			115	1067.	1067. 1067.	
55	111.4	111.4 111.4		116.6	111.8	(transition temperature)	tempera-
60	140.2		140.9 (38)	Solid phase: CuSO ₄ ·H ₂ O			
65	174.7			120	1232.		
70	216.2		215.5 (38)	125	1432.	1435. 1439.	
75	265.8						
80	323.8		320.6 (38)				
85	391.8	390.8 391.7 465.6 466.7					
90	466.8		464.9 (38)				
CuSO ₄ ·5H ₂ O ⇌ CuSO ₄ ·3H ₂ O + 2H ₂ O							
25	7.82*	7.82 7.82	7.5 (44) 7.77 (22) 7.78 (35) 7.8 (6) 7.92 (29)	55	60.18		
				60	81.58		83.4 (6) 80.8 ± 1.5 (23)
				65	109.8		
				70	146.0		
30	11.30	11.30 11.30		75	192.9		
				80	252.8		
35	16.14		16.3 (20)	85	328.8		
40	22.77			90	424.8*	424.6 424.6	432.7 (6)
45	31.81			95	544.8		
50	43.97	44.2 44.0	44.9 (6)	95.88	568.7	(transition temperature)	tempera-
CuSO ₄ ·3H ₂ O ⇌ CuSO ₄ ·H ₂ O + 2H ₂ O							
25	5.18*	5.09 5.20	5.6 (6) 4.7 (11) 4.5 (44)	70	104.0		
				75	138.4		
				80	182.8		182. (6)
30	7.58	7.60 7.60		85	238.7		
				90	310.8		
35	10.88	10.9 10.7	11.7 (6) 10.73 (20)	95	400.7		
				100	513.8	511.4 516.8	
40	15.50			105	654.0		
45	21.82		22.0 (6)	110	827.4	837.5 831.8	
50	30.40	30.3 30.8	30.3 (6)	115	1040.*	1023. 1038.	
55	41.92			116.6	111.8	(transition temperature)	tempera-
60	57.27						
65	77.52		77.1 (6)				

TABLE 2b

Aqueous vapor and dissociation pressures of barium chloride hydrate systems

t IN °C.	P CALCD.	P OBSD.	P (FOUND BY OTHERS)	t IN °C.	P CALCD.	P OBSD.	P (FOUND BY OTHERS)
BaCl ₂ , saturated solution							
Solid phase: BaCl ₂ ·2H ₂ O				100	639.7	639.7	(transition tempera- ture)
25	21.4		21.4 (39)	101.9	684.1	639.7	
30	28.6		28.6 (39)				
35	37.7		37.7 (39)	Solid phase: BaCl ₂ ·H ₂ O			
40	49.3		49.3 (39)				
45	63.8		63.8 (39)				
50	81.9		81.7 (39)	105	761.2		
55	103.9			110	901.6	901.6	
60	131.1					901.6	
65	163.5			115	1064.		
70	202.8			120	1292.		
75	249.5	249.5		125	1460.	1462.	
		248.9				1459.	
80	304.4			130	1690.	1687.	
85	369.7					1694	
90	445.9						
95	535.8	535.8					
		535.8					
BaCl ₂ ·2H ₂ O \rightleftharpoons BaCl ₂ ·H ₂ O + H ₂ O							
25	4.9 ₂	4.70 6.44	5.73 (1) 4.8 (11) 5.5 (35) 5.26 (28) 5.2 (12) 5.8 (44)	50	31.9 ₄	31.8 31.8	57.5 \pm 1. (23)
				55	44.7 ₃		
				60	62.0 ₉		
				60.1			
				65	85.2 ₉		
30	7.4 ₁			70	116.1		
33.8	9.9 ₂		10.0 (15)	75	156.7*	156.7	
35	10.8 ₆ *	10.9 11.8				156.7	
40	15.7 ₄		15.78 (1)	80	209.6		
45	22.5 ₄			85	277.7		
				90	366.1		
				95	478.4		
				100	621.2	620.9 620.9	
				101.9	684.1	(transition tempera- ture)	
BaCl ₂ ·H ₂ O \rightleftharpoons BaCl ₂ + H ₂ O							
50	1.3 ₁			90	30.5 ₂		
55	2.0 ₂			95	43.1 ₁		
60	3.0 ₉			100	60.3 ₂ *	60.4	
61.5	3.5 ₆		3.1 (15)			58.6	
65	4.6 ₈			105	83.7 ₅		
66.5	5.2 ₆		5.4 (15)	110	115.2	115.3	
70	6.9 ₃					116.4	
74.5	9.8 ₂		10. (15)	115	157.1		
75	10.2 ₁			120	212.7		
80	14.8 ₅			125	285.8*	280.5	
85	21.3 ₇					285.8	
				130	380.9		

TABLE 2c

Aqueous vapor and dissociation pressures of barium bromide hydrate systems

t IN °C.	P CALCD.	P OBSD.	P (FOUND BY OTHERS)	t IN °C.	P CALCD.	P OBSD.	P (FOUND BY OTHERS)
BaBr ₂ , saturated solution							
Solid phase: BaBr ₂ ·2H ₂ O				80	245. ₆		
				85	297. ₉	299.9	
25	17.8	17.8				299.2	
				90	358. ₉	358.9	
30	23.6	23.7				358.9	
				95	429. ₀		
35	31.1	23.6		100	511. ₇	507.0	
						510.5	
40	40.3	30.8		105	605. ₃	605.3	
						605.3	
45	52.0	52.1		107.9	664. ₂	(transition tempera- ture)	
50	66.3			Solid phase: BaBr ₂ ·H ₂ O			
55	84.2						
60	105. ₃			110	722. ₃	722.8	
65	132. ₁	131.5				727.8	
70	163. ₃	132.4		115	856. ₇		
				120	979. ₃		
75	201. ₁			125	115. ₁	1148.	
						1151.	
BaBr ₂ ·2H ₂ O ⇌ BaBr ₂ ·H ₂ O + H ₂ O							
25	3.7 ₃	2.71		70	85.9 ₆		
				75	115. ₉	116.9	
30	5.5 ₃	4.58				117.8	
35	8.1 ₀	7.82		80	154. ₃		
				85	205. ₁	205.1	
40	11.7 ₃	9.02				205.1	
43.3	14.5		10.0 (15)	90	270. ₀		
45	16.7 ₃			95	352. ₃		
50	23.7 ₄ *	23.4		100	457. ₃	460.3	
						465.6	
55	33.2 ₂	23.6		105	588. ₃ *	580.8	
60	46.0 ₃					582.1	
65	63.2 ₁	63.2		107.9	664. ₂	(transition tempera- ture)	
BaBr ₂ ·H ₂ O ⇌ BaBr ₂ + H ₂ O							
50	0.7 ₇			95	10. ₇		
55	1.0 ₃			100	13. ₃		
60	1.4 ₃			105	17. ₇		
65	1.9 ₃			110	22. ₃ *	22.5	
70	2.6 ₃			112.8	25. ₇		
75	3.6 ₁			115	28. ₄		
80	4.7 ₃			120	35. ₃		
85	6.3 ₀			125	44. ₇ *	44.7	
90	8.2 ₃			130	55. ₃		
							10.0 (15)

TABLE 2d

Aqueous vapor and dissociation pressures of strontium chloride hydrate systems

t IN °C.	P CALCD.	P OBSD.	P (FOUND BY OTHERS)	t IN °C.	P CALCD.	P OBSD.	P (FOUND BY OTHERS)
SrCl ₂ , saturated solution							
Solid phase: SrCl ₂ ·6H ₂ O				70	127. ₈		
25	17.0			75	157. ₆	157.8	
30	22.0	22.0				158.1	
		22.0		80	193. ₂		
35	28.4	28.4		85	235. ₃		
		28.4		90	285. ₄		
40	36.1			95	344. ₃		
45	45.3			100	414. ₀	414.0	
50	56.2	56.2				413.0	
		56.4		105	494. ₁		
55	69.3			110	584. ₉	583.4	
						583.4	
60	84.5	{ 84.7		115	687. ₄	{ 688.7	
		{ 84.5				{ 688.7	
61.34	88.4	{ transition temp. detd. by Richards		120	797. ₃		
		{		125	922. ₆	918.3	
61.6	89.7	{ trans. temp. from in- tersection of curves				922.6	
Solid phase: SrCl ₂ ·2H ₂ O				130	1047. ₇	1047.	
65	103. ₀	103.0				1047.	
		103.0					
SrCl ₂ ·6H ₂ O ⇌ SrCl ₂ ·2H ₂ O + 4H ₂ O							
25	8.3. ₂ *	8.32	8.37 (2)	45	32.7. ₀		
		8.37	7.5 (12)	50	44.8. ₁	44.2	
			8.4 (5)			45.0	
			8.52 (35)	55	60.7. ₉		
			6.35 (15)	60	81.7. ₈ *	82.0	
30	11.9. ₈					81.5	
35	16.8. ₉	16.8		61.34	88.3. ₇	Richards trans. temp.	
		17.1				{ trans. temp. from in-	
40	23.6. ₂			61.6	89.7. ₄	intersection of curves	
SrCl ₂ ·2H ₂ O ⇌ SrCl ₂ ·H ₂ O + H ₂ O							
25	1.9. ₀	2.14		85	105. ₉		
		2.01		90	139. ₈	136.1	
30	2.8. ₂					139.6	
35	4.1. ₈		2.09 (15)	95	182. ₄		
40	5.9. ₉			100	236. ₉ *	236.0	
45	8.5. ₈					237.7	
50	12.2. ₀ *	12.2		105	305. ₁		
		12.2		110	390. ₇	388.2	
						393.6	
55	17.0. ₄			115	496. ₈		
60	23.6. ₈			120	628. ₃		
65	32.4. ₉			125	790. ₁	803.5	
70	44.2. ₄					794.3	
75	59.7. ₂	59.7		130	987. ₂	975.0	
		59.3				997.7	

TABLE 2a

Aqueous vapor and dissociation pressures of strontium bromide hydrate systems

t IN °C.	P CALCD.	P OBSD.	P (FOUND BY OTHERS)	t IN °C.	P CALCD.	P OBSD.	P (FOUND BY OTHERS)
SrBr ₂ , saturated solution							
Solid phase: SrBr ₂ ·6H ₂ O				84.5	125. ₉	125.9	
25	14.0	14.0		85	105. ₇	125.6	
		14.0		85.5	123. ₃	123.0	
30	17.9					123.6	
35	22.8	22.8		88.0	118. ₂	(transition tempera- ture)	
		23.1					
40	28.8			Solid phase: SrBr ₂ ·H ₂ O			
45	35.9						
50	44.5	{ 44.6 44.4		90	128. ₆	128.5	
						130.3	
55	54.6			95	155. ₆	153.5	
60	66.6					155.6	
65	80.0	{ 80.0 80.0		100	187. ₁	185.4	
						189.7	
70	94.7			105	224. ₈		
75	111. ₂	110.7		110	268. ₆	266.1	
		111.4				263.0	
80	127. ₆	127.9		115	319. ₀		
		127.4		120	378. ₁		
				125	447. ₇	453.9	
						450.8	
SrBr ₂ ·6H ₂ O ⇌ SrBr ₂ ·H ₂ O + 5H ₂ O							
25	2.1 ₈ *	2.14		70	43.7 ₁		
		2.17					
30	3.1 ₆			75	58.2 ₂	56.6	
						58.8	
35	4.5 ₄	4.62		80	76.8 ₈		
		5.00					
40	6.4 ₇			85	100. ₆		
45	9.1 ₂			85.5	103. ₆ *	103.8	
						103.8	
50	12.7 ₂	12.5	12.0 (15)	86.5	109. ₁	108.9	
		12.8				108.9	
55	17.5 ₈			88.0	118. ₂	(transition tempera- ture)	
60	24.0 ₂						
65	32.5 ₈						

ments which were made at each temperature. One of these initial concentrations (tabulated above) was higher, the other (tabulated below) lower than the final concentration. In the third column are stated the relative aqueous pressures of acids of these final concentrations, taken from the

work already published (8). In the fourth column under P is stated the actual aqueous pressure in millimeters of mercury at 0°C . and standard gravity.

TABLE 2f

Aqueous vapor and dissociation pressures of calcium chloride hydrate systems

t IN $^\circ\text{C}$.	P CALCD.	P OBSD.	P (FOUND BY OTHERS)	t IN $^\circ\text{C}$.	P CALCD.	P OBSD.	P (FOUND BY OTHERS)
CaCl ₂ , saturated solution							
Solid phase: CaCl ₂ ·6H ₂ O				Solid phase: CaCl ₂ ·2H ₂ O			
25	6 7 ₃	6 73	6.7 (33)	50	15 4	15.4	15.5 (33)
		6.92	6.97 (16)			15.4	15.5 (16)
29	7.1 ₀	7.24	6 9 (33)	55	19.8		
		7.02	7.33 (16)	60	25.3		
30	7.0 ₃	7 24	6 7 (33)	65	32.1		
		7.03	6 88 (16)	70	40.2		
30	(transition temperature)			75	51 3	49 4	54.0 (33)
						49.4	51.3 (16)
Solid phase: CaCl ₂ ·4αH ₂ O				80	62.0		
				85	76 0		
35	8 6 ₅	8 65	8.6 (33)	90	92.9		
		9.02	8 63 (16)	95	112.4		
40	10 5	10.6	10 4 (33)	100	135.2	135.2	145. (33)
		10.4	10.53 (16)			135.2	138. (16)
45	11.7	11 7	11 7 (33)	105	161.7		
		11 7	11.9 (16)	110	192.8	192.8	
45.4	11 6 ₈	(transition temperature)				192.8	
				115	226.5		
				120	265.8		
				125	309.7	309.7	308. (16)
						309.7	
CaCl ₂ ·4αH ₂ O ⇌ CaCl ₂ ·2H ₂ O + 2H ₂ O							
25	2 5 ₆ *	2.58	3 4 (33)	40	7.9 ₆	7.93	8.5 (33)
		2 56				8.19	
30	3 7 ₉	3 66	4.6 (33)	45	11 3 ₆ *	11 3	11.0 (33)
		3 61				11.5	
35	5 5 ₃	5 47	6 3 (33)	45 4	11.6 ₈	(transition temperature)	
		5.66					

INTERPOLATION, SMOOTHING, AND TABULATION OF RESULTS

In order to obtain values for temperatures other than those observed and to smooth the observed values we used two methods (A and B).

Method A. For dissociation pressures of the salt hydrate systems an equation of the form

$$\log_{10} P = A - B/T \quad (N)$$

fits the observations sufficiently well over our temperature ranges. In selecting constants for such equations, smaller weight was given to lower temperature observations which were less reliable for the reasons advanced above. The pressure values yielded for 5°C. intervals by the equations are shown under "*P* calcd." in the second columns of tables 2a to 2f, where the two starred pressures are those used in defining the straight line; these are followed in the third columns by our observed values, two for each temperature studied, in the order stated above; and in the fourth columns by values observed by other investigators. In table 3 are shown the values of the constants *A* and *B* of the above equation for the hydrates studied, and also the latent heat of vaporization, *L*, per mole of water as derived from these equations with the customary simplifying assumptions.

Method B. For saturated salt solutions it is not usually possible to represent the facts by an equation of the type *N*. This is at once apparent

TABLE 3

Constants for the type N equations and the latent heats of vaporization per mole of water

SYSTEM	<i>A</i>	<i>B</i>	<i>L</i> CALCULATED
CuSO ₄ ·5—3H ₂ O	10.5844	2888.93	13.2 ₉
CuSO ₄ ·3—1H ₂ O	10.6446	2960.15	13.5 ₆
BaCl ₂ ·2—1H ₂ O	11.1212	3107.24	14.2 ₉
BaCl ₂ ·1—0H ₂ O	12.5305	4010.70	18.4 ₅
BaBr ₂ ·2—1H ₂ O	10.9623	3097.51	14.1 ₇
BaBr ₂ ·1—0H ₂ O	9.2600	3029.47	13.9 ₄
SrCl ₂ ·6—2H ₂ O	10.3525	2811.35	12.9 ₂
SrCl ₂ ·2—1H ₂ O	10.7065	3108.73	14.3 ₀
SrBr ₂ ·6—1H ₂ O	10.3020	2971.73	13.6 ₇
CaCl ₂ ·4α—2H ₂ O	10.6918	3065.43	14.1 ₀

when one learns that the curves representing the experimental results plotted with log *P* as ordinate and 1/*T* as abscissa sometimes exhibit a maximum. This has been observed by three earlier workers (39, 10, 33) and was found by us in two cases, those of saturated solutions of CaCl₂·6H₂O and of SrBr₂·6H₂O. When no maximum appears, the curvature nevertheless often changes more rapidly as a transition temperature is approached. The reason for this may be appreciated on recalling that the slope of such a curve is proportional to the work of removing liquid water from the solution and converting it to vapor. In the case of a saturated salt solution, removal of water necessitates concomitant deposition of solid salt, a process in which energy may enter the system, so that the work for vaporization, considered as a whole, may legitimately become zero or change sign.

For this reason we were obliged to use graphical interpolation and smoothing. Instead of interpolating directly from the smoothed curves

of $\log P$ versus $1/T$ a more sensitive method was used. In this method the pressures at the observed temperatures are calculated on the temporary

TABLE 4
Heats of vaporization per gram of water from the saturated solutions

t in °C.	H ₂ O	CuSO ₄ ·5H ₂ O	BaCl ₂ ·2H ₂ O	BaBr ₂ ·2H ₂ O	SrCl ₂ ·6H ₂ O	SrBr ₂ ·6H ₂ O	CaCl ₂ ·6H ₂ O
25	583	557	583	552	521	486	249
28.5	581						0
30	580						-81
							CaCl ₂ ·4H ₂ O
35	577						449
45	572						246
							CaCl ₂ ·2H ₂ O
50	569	553	561	550	489	467	575
60	564				476		
					SrCl ₂ ·2H ₂ O		
65	561	540	540	550	545	379	571
75	555				546		
82.3	550					0	
87	548					-261	
						SrBr ₂ ·H ₂ O	
90	546	488				529	
95	543						
		CuSO ₄ ·3H ₂ O					
100	540	507	540	521	540	548	570
			BaCl ₂ ·H ₂ O				
105	537		543	506			
				BaBr ₂ ·H ₂ O			
110	533	502		513			
115	530						
		CuSO ₄ ·H ₂ O					
120	526	517	522	515	453	614	515
125	523	515					

assumption that $\log P$ is a linear function of $1/T$. This assumption not being true, there was a difference between the logs of the observed pressures and those so calculated. These differences were plotted as a function of

the temperature, and by the aid of the smooth curve connecting them the pressures were calculated for intervals of 5°C .

To obtain for the saturated solutions approximate values for Q , the heat of vaporization per gram of water, we made use of the relation already discussed in the case of sulfuric acid (8). The values of Q at various

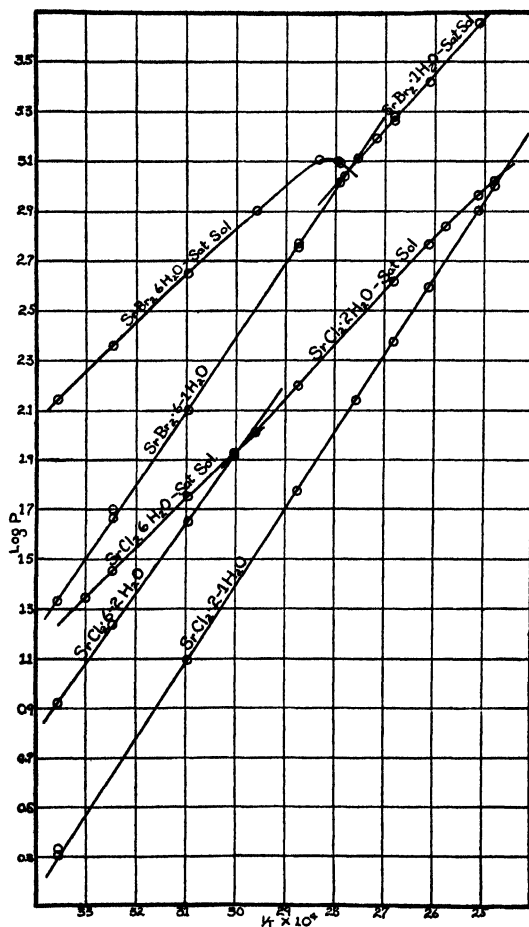


FIG. 2. Aqueous vapor and dissociation pressures in the systems strontium bromide-water and strontium chloride-water. (For the strontium bromide-water system subtract 1.0 from the $\log P$ scale.)

temperatures as arrived at in this way are set down in table 4, which shows the changes which take place in Q in the vicinity of a transition point. Q for water is given for comparison.

Because of the interest of their dissimilarity, graphs with $\log P$ as ordinates and $1/T$ as abscissas are exhibited in figure 2 for both aqueous

pressures of saturated solutions and for dissociation pressures of the solid hydrates in the two systems strontium chloride and strontium bromide with water.

DISCUSSION OF ERROR

Sufficient data have been presented here and elsewhere (8) to enable one to make stepwise an estimate of a minimum probable error for an individual reported value of pressure, but it is more practical to compare the actual results of a number of duplicate experiments. When this is done, and the improvement due to smoothing taken into account, it is seen that errors in the tabulated smoothed values of pressures should, unless at low pressures, seldom exceed by 1 per cent the percentage errors of the published (16) vapor pressures of water which were taken as standard. We are encouraged to believe that serious systematic error is absent because of our essential agreement with the best results of a few others who have used different methods with due precaution.

REMARKS ON THE INDIVIDUAL SYSTEMS AND THEIR TRANSITION TEMPERATURES

Cupric sulfate. Our observations are not sufficiently numerous to indicate a transition in the pentahydrate at $56^{\circ}\text{C}.$, as reported by Cohen (7). The values quoted in table 2a for Wilson's observations are the values of aqueous pressure corresponding to his stated equilibrium concentration of sulfuric acid as converted by the table published by Collins (8), and not from Wilson's similar table (45). We determined the transition temperature of pentahydrate to trihydrate by the heat effect, using a method similar to that of Richards and Yngve (31), and measuring temperature by a platinum resistance thermometer. Sharp arrests were obtained both on heating and on cooling at $95.88 \pm 0.02^{\circ}\text{C}.$ This is in agreement with the point of intersection at $95.9 \pm 0.1^{\circ}\text{C}.$ of the dissociation pressure curve of the pentahydrate with the vapor pressure curve of the saturated solution. International Critical Tables give $95.7 \pm 0.2^{\circ}\text{C}.$ The transition temperature between tri- and monohydrate is defined as $116.6 \pm 0.2^{\circ}\text{C}.$ by the point of intersection of our curve for the dissociation pressure of the trihydrate with the vapor pressure curve of the saturated solution.

Barium chloride. The transition temperature between the di- and the monohydrate was directly determined from the heat effect as above described, and found to be at $101.94 \pm 0.05^{\circ}\text{C}.$, in agreement with the intersection of the appropriate aqueous vapor curves at $101.9 \pm 0.1^{\circ}\text{C}.$ For the dissociation pressure of the monohydrate values of 2.5 (11), 2.4 (25), 2.9 (28), and 1.1 mm. (34) have been reported for $25^{\circ}\text{C}.$ These values are presumably all high, for the reasons outlined above. Extrapolation of our rectilinear relation yields only 0.12 mm.

Barium bromide. Direct determination by the heat effect of the transi-

tion temperature between di- and monohydrate yielded $107.91 \pm 0.05^\circ\text{C}$., while the appropriate aqueous pressure curves cut at $108.0 \pm 0.1^\circ\text{C}$. The values given for the dissociation pressures of the monohydrate are tentative, since equilibrium was attained from only one direction.

Strontium chloride. The transition temperatures at 61.6°C . and 132.5°C . found, the latter by extrapolation, from the intersection of the appropriate aqueous pressure curves are in only fair agreement with the values of Richards and Yngve (31) at 61.34°C . and of Menzies (unpublished work on solubility) at 135.6°C ., respectively.

Strontium bromide. There has been uncertainty in the literature as to the existence of a dihydrate. Richards and Yngve believed that the transition which, as a preliminary result, they set at 88.62°C . was from hexahydrate to, possibly, dihydrate. In dehydration experiments we found no evidence for a dihydrate. Repeating their determination of the transition point, we obtained $88.0 \pm 0.1^\circ\text{C}$., and found by analysis that the product of the transition was the monohydrate. Of a series of samples which we dehydrated so as to obtain products of gross analysis corresponding to 4.5, 3.5, 2.5, 1.8, 1.3 and 0.6 H_2O with SrBr_2 , all gave identical dissociation pressures except the last, whose pressure was lower. Since our work was completed, the same conclusion as to the absence of a dihydrate has been reached by others (15).

Calcium chloride. The transition temperatures as tabulated were arrived at from curve intersections, and are in good agreement with the values given in International Critical Tables.

SUMMARY

An isopiestic method has been described for measuring aqueous vapor and dissociation pressures by equilibration with aqueous sulfuric acid solutions.

Because the aqueous pressures of the reference solution vary with temperature in a manner very similar to that of the substance under investigation, the need for close constancy of long-continued temperature control is much relaxed in stringency, and this makes for experimental simplicity especially at temperatures above 100°C .

Experiments are conducted in common test tubes which are sealed, thus offering no greater difficulty for pressures above one atmosphere than below.

To illustrate the unusual breadth of range in temperature and pressure thus made easily accessible, six salt hydrate systems were examined and reported upon for temperatures up to 130°C . These include, in anhydrous and various hydrated forms, the chlorides of barium, strontium, and calcium, the bromides of barium and strontium, and cupric sulfate. For each salt pressure equilibrium values have been tabulated for the various univariant and many of the invariant systems formed with water.

Heats of vaporization of water from the several hydrates and from their saturated solutions have been evaluated.

Causes for difficulty of attaining true equilibrium values in such measurements have been discussed.

REFERENCES

- (1) BAXTER AND COOPER: J. Am. Chem. Soc. **46**, 923 (1924).
- (2) BAXTER AND LANSING: J. Am. Chem. Soc. **42**, 419 (1920).
- (3) BAXTER AND STARKWEATHER: J. Am. Chem. Soc. **38**, 2038 (1916).
- (4) BOLTE: Z. physik. Chem. **80**, 348 (1912).
- (5) BOLTE: Z. physik. Chem. **36**, 517 (1901).
- (6) CARPENTER AND JETTE: J. Am. Chem. Soc. **45**, 578 (1923).
- (7) COHEN: Z. physik. Chem. **31**, 172 (1899).
- (8) COLLINS: J. Phys. Chem. **37**, 1191 (1933).
- (9) CROWTHER AND COUTTS: Proc. Roy. Soc. London **106A**, 215 (1924).
- (10) DERBY AND YNGVE: J. Am. Chem. Soc. **38**, 1439 (1916).
- (11) FOOTE AND SCHOLES: J. Am. Chem. Soc. **33**, 1309 (1911).
- (12) FROWEIN: Z. physik. Chem. **1**, 5, 362 (1887).
- (13) HACKSPILL AND KIEFFER: Ann. chim. [10] **14**, 227 (1930).
- (14) HOLLMANN: Z. physik. Chem. **37**, 193 (1901).
- (15) HÜTTIG AND SLONIM: Z. anorg. allgem. Chem. **18**, 65 (1929).
- (16) International Critical Tables, Vol. III, p. 367. McGraw-Hill Book Co., New York (1928).
- (17) JETTE: Private communication.
- (18) LANGMUIR: Gen. Elec. Rev. **25**, 445 (1922).
- (19) LINEBARGER: Z. physik. Chem. **13**, 500 (1894).
- (20) LOGAN: J. Phys. Chem. **36**, 1035 (1932).
- (21) LOEWENSTEIN: Z. anorg. allgem. Chem. **63**, 69 (1909).
- (22) MENZIES: J. Am. Chem. Soc. **42**, 1951 (1920).
- (23) MENZIES AND HITCHCOCK: J. Phys. Chem. **35**, 1660 (1931).
- (24) MENZIES AND POTTER: J. Am. Chem. Soc. **34**, 1452 (1912).
- (25) MUELLER-ERZBACH: Z. physik. Chem. **2**, 113, 546 (1888).
- (26) MURRAY: Standards and Tests for Reagent Chemicals. D. Van Nostrand Co., New York (1920).
- (27) NOYES AND WESTBROOK: J. Am. Chem. Soc. **43**, 726 (1921).
- (28) PARTINGTON: J. Chem. Soc. **99**, 466 (1911).
- (29) PARTINGTON AND HUNTINGFORD: J. Chem. Soc. **123**, 160 (1923).
- (30) RICHARDS: J. Am. Chem. Soc. **31**, 6 (1909).
- (31) RICHARDS AND YNGVE: J. Am. Chem. Soc. **40**, 89 (1918).
- (32) ROBERTS AND BURY: J. Chem. Soc. **123**, 2037 (1923).
- (33) ROOZEBOOM: Z. physik. Chem. **2**, 449 (1888); **4**, 31, 44 (1889).
- (34) SCHOTTKY: Z. physik. Chem. **64**, 415 (1908).
- (35) SCHUMB: J. Am. Chem. Soc. **45**, 342 (1923).
- (36) SIDGWICK AND EUBANK: J. Chem. Soc. **125**, 2273 (1924).
- (37) SMITH AND MENZIES: J. Am. Chem. Soc. **32**, 1412 (1910).
- (38) SPERANSKI: Z. physik. Chem. **78**, 101 (1912).
- (39) SPERANSKI: Z. physik. Chem. **78**, 86 (1912).
- (40) THOMAS AND BARKER: J. Chem. Soc. **127**, 2920 (1925).
- (41) THOMAS AND RAMSAY: J. Chem. Soc. **123**, 3256 (1923).
- (42) TOPLEY AND SMITH: J. Chem. Soc. **147**, 321 (1935).
- (43) VAN BEMMEL: Z. anorg. allgem. Chem. **13**, 233 (1897).
- (44) WILSON: J. Am. Chem. Soc. **43**, 704 (1921).
- (45) WILSON: Ind. Eng. Chem. **13**, 326 (1921).

A NEW ELECTROPHORESIS CELL FOR MICROSCOPIC OBSERVATIONS^{1,2}

MARGARET E. SMITH AND MARTIN W. LISSE

*Department of Agricultural and Biological Chemistry, The Pennsylvania State College,
State College, Pennsylvania*

Received August 31, 1935

PART I. DESCRIPTION, THEORY, AND THEORETICAL ADVANTAGES OF THE NEW CELL

Recent electrophoretic studies have involved the use of closed type cells, of either rectangular or circular cross section. The theory and use of such cells have recently been reviewed by Abramson (1). In both of these types the liquid returns along the axis of the cells, the velocity of the liquid being a parabolic function of the depth. The actual electrophoretic velocity can be obtained from observations at certain depths. However, at these depths the velocity gradient is large; the observed velocity changes rapidly with depth, and inaccuracy results.

The new cell described in this paper consists of two tubes in parallel between the electrodes, the dimensions of the tubes having a relation such that return flow takes place only through the tube of larger radius; there is no movement of the liquid along the axis of the tube of smaller radius, hence the velocities observed at the one-half depth in this tube are the actual electrophoretic velocities. At this depth the velocity gradient is zero, so that a slight inaccuracy in determining the depth of observation produces no appreciable change in the observed velocity of the particles.

DESCRIPTION OF APPARATUS

Diagrams of the apparatus are shown in figure 1. The essential parts of the apparatus are two fused quartz tubes, T_1 and T_2 , used in parallel, two end tubes having stopcocks for filling the apparatus, and electrodes.

The dimensions of these two quartz tubes should have the relation

$$L_2/L_1 = A^2(A^2 - 2)$$

¹ The data in this paper are taken from a thesis submitted by Margaret E. Smith to the Faculty of the Pennsylvania State College in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1935.

² Authorized on July 27, 1935 for publication as Paper No. 698 in the Journal Series of the Pennsylvania Agricultural Experiment Station.

where $A = R_2/R_1$, and L_2 , L_1 , R_2 , and R_1 are the lengths and radii of tubes T_2 and T_1 , respectively. The development of this equation is given in the section concerned with the theory of the cell.³

The procedure followed to obtain tubes of the correct dimensions was as follows: Tube 1 was ordered according to certain specifications,⁴ viz., a capillary tube of good optical quality fused quartz, outer diameter approximately 3 mm., bore 0.5–0.7 mm., three sides of the tube to be ground off giving two parallel planes and one at right angles to these, thus allowing for observation, and for illumination either from the side or from underneath as desired. A diagram of the cross section of the tube is also shown in

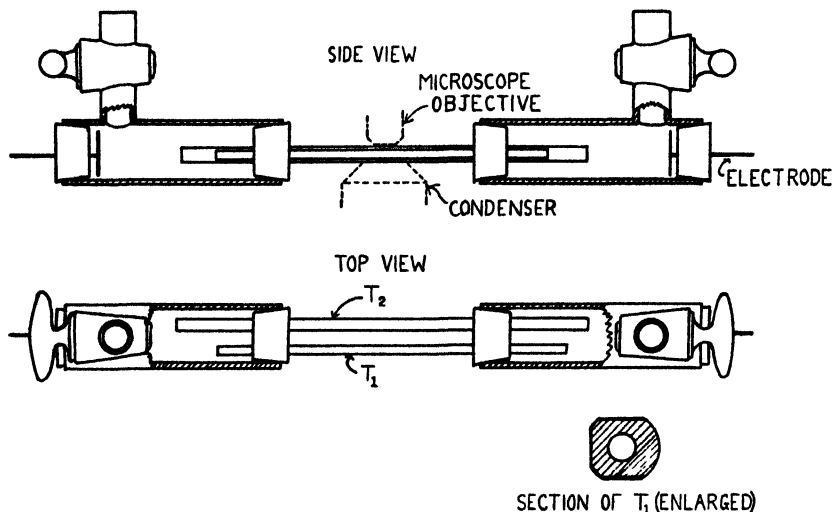


FIG. 1. Diagrams of the new double-tube cell for determination of electrophoretic mobilities

figure 1. The dimensions permissible for the cross section of this tube are limited by the working distance of the optical equipment to be used.

The bore of tube 1 was carefully determined by calculation from the length and weight of a column of mercury placed in the tube. Then a length of tubing was ordered from the stock supply of fused quartz tubing, with the specification that its bore should be uniform, and within the range of 1.5 to 1.6 times that of tube 1. The bore of this tube was determined in the same manner as described for tube 1, and the desired length cut off for tube 2.

³ The authors are indebted to Dr. Turner L. Smith of the Carnegie Institute of Technology, Pittsburgh, Pennsylvania, for the suggestion of the new cell and development of the theory concerning it.

⁴ The quartz tubes were obtained from the Thermal Syndicate, Ltd., Brooklyn, New York.

Thus, if T_1 has a length of 10 cm., a radius of 0.3 mm., and T_2 has a radius of 0.48 mm., the length of T_2 is given by

$$L_2 = 10 \times 1.6^2(1.6^2 - 2)$$

or $L_2 = 14.34$ cm.

It is essential that tubes 1 and 2 be of the same material, since development of the theory of the cell assumes like surface conditions in the two tubes. Quartz was selected for these tubes, since (a) an optically good plane surface can be obtained through grinding and polishing of the quartz, and (b) the indices of refraction of quartz and water are more alike than those of glass and water, hence there should be less distortion of the images.

The quartz tubes were then inserted into two-hole rubber stoppers, making sure that the two tubes were far enough apart so that the larger tube would not interfere with the use of the objective and condenser on the microscope, and sealed into the stoppers with deKhotinsky cement.

The end tubes were of Pyrex glass tubing, with Pyrex glass stopcocks added for filling. The exact dimensions used are not important; in this case the length was approximately 12 cm. and the bore 1.8 cm.

The electrodes used were circular platinum disks, with wires attached leading through the rubber stoppers for connecting to the source of potential. In case solutions are used in which polarization occurs readily, non-polarizable electrodes should be used.

OPERATION OF CELL

Operation of the cell involves the same technic as in the operation of other cells for microscopic observation of electrophoretic movement, except that the microscope is focused on the one-half depth in the tube of smaller radius. Hence the procedure is discussed here only in brief.

An apparatus resting on three leveling screws was built for holding the cell; this gave a simple means of adjustment for getting the plane of the cell parallel to the surface of the condenser. After the cell is filled with suspension and placed in position the electrodes are connected to the source of potential. A double-throw switch allows for frequent reversal of the current, thus preventing polarization. A milliammeter may be connected in series with the cell if desired.

The mobility of the particles (velocity per unit potential gradient) can be determined if the potential gradient is known. Since the radii of tubes T_1 and T_2 are much less than the radii of the end tubes, for most work the fall of potential through the end tubes can be neglected. Then the potential gradient through the tube where observation is made is given by E/L_1 , where E is the total fall in potential between the electrodes, measured with a voltmeter in parallel with the cell, and L_1 is the length of T_1 .

If a greater degree of accuracy is warranted, the potential gradient can be calculated more exactly from the dimensions of the apparatus. The use of this method in reference to electrophoretic cells is discussed by Northrop (3). Measurement of the current allows for another method of calculating the potential gradient; this method is discussed by Abramson (1).

For cleaning the apparatus, the rubber stoppers are removed from the end tubes. The two quartz tubes are left sealed in the two-hole stoppers. These tubes can be filled with water, alcohol, ether, or cleaning solution as desired with the aid of a hypodermic syringe; also, if desired, a small wire (insulated, thus preventing scratching of the surface) can be passed through the tubes. The end tubes and the electrodes are also cleaned. Thorough rinsing of the apparatus is very important, since small traces of electrolytes markedly affect electrophoretic potentials.

THEORY OF THE CELL

1. *General theory of electrosmotic flow in tubes*

The theory of electrophoresis cells assumes that the liquid is electrically neutral except for a charged layer lying very close to the wall of the cell. The electric field which is applied causes motion in this layer; this is defined as electrosmosis. Owing to the viscosity of the fluid, the motion of this layer induces a motion of the entire fluid in the cell. This motion is assumed to be both steady and nonturbulent.

The theory of tubular electrophoresis cells may be derived in the following manner. Consider the portion of the liquid inside a cylinder coaxial with the tube but of smaller radius. Electrosmotic movement of the liquid results in a difference in pressure at the ends of the tubes; the resultant force acting on the ends of the cylindrical portion of the fluid is just balanced by the shearing stress on the cylindrical surface, caused by the viscosity and thus proportional to the rate of change of velocity with the radius. This balance is expressed by the equation

$$2\pi r L \eta \frac{dv_w}{dr} = \pi r^2 P$$

which gives on integration

$$v_w = \frac{P}{4\eta L} r^2 + C \quad (1)$$

in which v_w denotes the velocity of the liquid, P the difference in hydrostatic pressure at the ends of the tube of length L , η the coefficient of viscosity of the liquid, and r the radius of the tube of flow being considered. This equation is the fundamental equation for flow of liquids in tubes; its development is found in treatises concerned with hydrodynamics of liquids (see Lamb (2)).

In the case being considered, the constant C can be evaluated from the condition that the velocity of the liquid at the wall of the tube is the electrosmotic velocity; that is, when $r = R$, $v_w = V_e E/L$, where R denotes the radius of the tube, V_e the electrosmotic mobility of the liquid, E the applied electromotive force, and L , as above, is the length of the tube. Hence equation 1 becomes

$$v_w = \frac{P}{4\eta L} (r^2 - R^2) + \frac{V_e E}{L} \quad (2)$$

The total volume, W , of liquid transported per unit time across any section is given by

$$W = \int_0^R v_w \cdot 2\pi r \, dr$$

Substituting in this the value of v_w given in equation 2, and integrating, we obtain

$$W = \pi R^2 \left(\frac{V_e E}{L} - \frac{PR^2}{8\eta L} \right) \quad (3)$$

Equations 2 and 3 are the general equations for the velocity of electrosmotic flow of liquids and the volume of liquid transported by electrosmosis in cylindrical tubes.

2. Theory of electrophoresis in a single closed tube

The observed velocity, V_{obsd} , of a particle at any depth in the tube will be the sum of the actual electrophoretic velocity, U , and the velocity of the liquid, i.e.,

$$V_{\text{obsd.}} = U + v_w \quad (4)$$

In a single closed tube, the total volume of liquid transported in one direction is zero. When $W = 0$, from equations 2 and 3 we obtain the equation for the velocity of the liquid in a closed tube

$$v_w = \frac{P}{4\eta L} \left(r^2 - \frac{R^2}{2} \right) \quad (5)$$

The depths at which there is no movement of the liquid are found by setting $v_w = 0$ in equation 5; this gives

$$r = \pm \frac{R}{2} \sqrt{2}$$

Focusing at these depths, the observed velocity is the actual electrophoretic velocity of the particles.

Actual electrophoretic velocities can also be obtained in another manner, thus,

$$\int_0^R V_{\text{obsd.}} \cdot 2\pi r \, dr = \int_0^R U \cdot 2\pi r \, dr + \int_0^R v_w \cdot 2\pi r \, dr \quad (6)$$

In a closed tube the total volume of liquid transported, represented by the last term in the preceding equation, is zero; hence equation 6 becomes

$$U = \frac{2}{R^2} \int_0^R V_{\text{obsd.}} \cdot r \, dr \quad (7)$$

Therefore, by taking readings at various depths in the cell, an approximation of the actual electrophoretic velocity can be obtained.

By substituting $r = 0$ and $r = R$ in turn in equation 5, it appears that the velocity of the liquid at the axis of the tube is equal in magnitude but opposite in direction to the velocity of the liquid at the wall of the tube, i.e., to the electrosmotic velocity, $V_e E/L$. Hence by use of equation 4 we obtain

$$V_e E/L = U - V'_{\text{obsd.}} \quad (8)$$

where $V'_{\text{obsd.}}$ is the observed particle velocity in the single tube cell at depth $r = 0$. Thus the electrosmotic velocity can be calculated if the observed particle velocity at the one-half depth and the electrophoretic velocity are known.

3. Theory of cell consisting of two tubes in parallel

Consider two tubes of different radii in parallel between two electrodes. Let T_1 denote the tube of smaller radius, and T_2 that of larger radius. The general equations 2 and 3 for the velocity and volume of liquid transported apply; subscripts will be used to refer to the dimensions of these two tubes, as L_1 for the length of T_1 , R_1 its radius, etc. The actual electrosmotic mobility, V_e , will be the same in both tubes, since the tubes are of the same material; also, the applied E.M.F. and the difference in pressure, denoted by E and P , respectively, will be the same in both tubes.

The total volume of liquid transported in one direction in the two tubes is zero; hence from equation 3 we obtain

$$W = \frac{\pi R_1^2}{L_1} \left(V_e E - \frac{PR_1^2}{8\eta} \right) + \frac{\pi R_2^2}{L_2} \left(V_e E - \frac{PR_2^2}{8\eta} \right) = 0 \quad (9)$$

We wish to determine conditions such that there will be no movement of liquid along the axis of the smaller tube. The velocity at this depth can be obtained by setting $r = 0$ in equation 2. This gives

$$v_w \text{ along axis of } T_1 = -\frac{PR_1^2}{4\eta L_1} + \frac{V_e E}{L_1} \quad (10)$$

When this velocity = 0,

$$V_e E = \frac{PR_1^2}{4\eta} \quad (11)$$

This value substituted in equation 9 gives on simplification

$$R_1^4 L_2 + 2R_2^2 R_1^2 L_1 - R_2^4 L_1 = 0$$

Solving this for L_2 ,

$$L_2 = \frac{L_1(R_2^4 - 2R_1^2 R_2^2)}{R_1^4} \quad (12)$$

Let the ratio of the radii, R_2/R_1 , be denoted by A . Then equation 12 can be written in the form,

$$L_2/L_1 = A^2(A^2 - 2) \quad (13)$$

If tubes are used whose dimensions satisfy the relations given in equation 13, there will be no movement of liquid along the axis of the smaller tube; velocities observed at this depth will be the actual electrophoretic velocities of the particles.

THEORETICAL ADVANTAGES OF THE NEW CELL

According to the development of the theory as given, velocity of liquid in tubes due to electrosmosis is a parabolic function of the depth; this is evident from the general equation 2, which is of the type $v_w = Ar^2 + B$, the constants A and B being dependent on conditions in the tubes used.

Equation 5 gives the equation for velocity of liquid in a single closed tube. This is a parabola, with the velocity at the maximum equal in magnitude but opposite in direction to the electrosmotic velocity of the liquid. Curves for cylindrical tube type cells are given by Abramson (1). At depths given by

$$r = \pm \frac{R}{2} \sqrt{2}$$

at which actual electrophoretic velocities are obtained, the velocity gradient (change in velocity with depth) is large; hence inaccurate results are obtained if a slight error in focusing is made.

The same condition is present at the levels used for observation in a single cell of rectangular cross section; in such a cell velocities are obtained at approximately the one-fifth and four-fifths depths, at which depths velocity changes rapidly with depth.

For the new cell the condition was stipulated that there should be no movement of the liquid at the axis of the tube of smaller radius. The velocity of the liquid in this tube expressed as a function of the radius can be obtained from equations 2 and 11; this is

$$v_w = Pr_1^2/4\eta L_1$$

This corresponds to a parabola with the maximum at the points where $r = 0$, and $v_w = 0$. It is evident that the velocity gradient, dv_w/dr_1 , is also zero at this point.

The observed velocity of the particles is the algebraic sum of the electrophoretic velocity and the velocity of the liquid. Assuming that the electrophoretic velocity is constant, it is evident that the $V_{\text{obsd.}}$ -depth curve is a parabola of the same general form as the v_w -depth curve; the coördinates of the maximum for this curve in the new cell are $r = 0$ and $V_{\text{obsd.}} = U$, and the velocity gradient at this point is zero.

Theoretical advantages of the new cell in comparison with a single tube cell are dependent on the fact that electrophoretic velocities are determined at the maximum of the velocity observed-depth curve. They may be listed as follows: (a) The proper depth for observation is readily found; since observations are made at the depth where the particle velocity is greatest, a few readings above and below this depth aid in checking the correct level. (b) A slight error in focusing does not result in appreciable errors in velocities, since change in velocity with depth is small at points near the correct level. (c) Depth of field of view is not as important a factor as in the case of a single closed tube, in which particles at a slightly different level have noticeably different velocities. (d) Rotational effects on particles are at a minimum, since the velocity gradient near the level of observation is small. This particular advantage suggests the use of a cell of this type for studies on larger particles where the effect of change in velocity with depth is a factor which must be considered.

SUMMARY

1. A new electrophoresis cell for microscopical observations of particle velocities is described; this consists of two tubes in parallel between the electrodes. By extension of the general theory of electrosmotic flow of liquid in tubes, it is shown that the flow of liquid at the one-half depth in the tube of smaller radius can be eliminated if the dimensions of the two tubes have a definite relation to each other. Hence, the observed particle velocities at this depth are the actual electrophoretic velocities, from which the mobilities can be calculated.

2. In this new cell electrophoretic velocities are given at the maximum of the parabolic curve expressing velocity as a function of depth. Advantages resulting thereby are: (a) Difficulty in focusing is alleviated, since

the observed velocity is a maximum at the correct level. (b) Slight errors in focusing, or errors due to depth of field of view of the microscope, are less important than in a single tube cell, since the velocity gradient is small near the correct level of observation. (c) Rotational effects of the liquid are less in the case of the new cell, since change of velocity with depth is at a minimum at the depth of observation.

PART II. EXPERIMENTAL COMPARISON OF THE NEW CELL AND A CYLINDRICAL TUBE CELL

As a means of confirming the theory and construction of the new cell, the electrophoretic mobility of quartz particles in distilled water was determined by three different methods, as follows: (a) In the new cell, actual electrophoretic mobilities being determined from observations at the one-half depth in the tube of smaller radius. (b) In a single-tube cell, actual mobilities being obtained from observations at depths where theoretically there should be no movement of the liquid. (c) In a single-tube cell, observing at various depths, and obtaining an approximate value for the electrophoretic mobility.

EXPERIMENTAL PROCEDURE AND RESULTS

General technic

Pieces of quartz tubing (the same material as used in the quartz tubes of the new electrophoresis cell) were cleaned with cleaning solution, thoroughly rinsed with distilled water, then with triply distilled water, dried, and ground in an agate mortar. A suspension of this powder was made in triply distilled water; this was allowed to settle for about four hours, after which the upper portion was siphoned off and used for the experiments. The quartz particles in this portion of the suspension were therefore small enough to stay suspended for some time.

Observation was made in T_1 (see description of the new cell given in Part I), used either as a single-tube cell or in parallel with T_2 . The cell was carefully cleaned before using, and thoroughly rinsed, including two rinsings with triply distilled water previous to filling with the suspension. The optical combination consisted of a 10x ocular, a 21x (8 mm. 0.50) objective, and a cardioid condenser giving dark-field illumination. Observations of the velocities were made and mobilities calculated, the potential gradient being given with sufficient accuracy by E/L_1 , where E is the applied E.M.F. and L_1 is the length of T_1 . Experiments were carried out at room temperature and corrected to a temperature of 25°C. on the assumption that electrophoretic velocity varies inversely as the viscosity of the medium, i.e., $U\eta = \text{constant}$. This would appear probable for suspensions of quartz particles, at least for the small range of temperature (25–29°C.) concerned in the experiments.

Series I

Six experiments were carried out using the new cell. Each experiment consisted of one hundred observations on a suspension of quartz particles prepared as previously described; the current was reversed in order to prevent polarization after each set of five readings, the microscope re-focused after twenty readings, and the cell refilled with fresh suspension after sixty readings. The mobilities were calculated, and the arithmetic mean (A.M.) and standard deviation (S.D.) of the values determined; these values were then corrected for a temperature of 25°C.

TABLE 1

Electrophoretic mobilities of quartz particles in distilled water at 25°C. as determined at depths where there was no movement of the liquid in the new cell, and in a single-tube cell

EXPT. NO.	A M * AND S.D † OF MOBILITIES IN μ /SEC /VOLT/CM.			
	Series I—New cell		Series II—Single-tube cell	
	A.M.	S.D.	A M.	S D.
1	3.55	0.24	2.84	0 60
2	2.93	0.31	2.76	0 63
3	3.07	0.21	3 56	0 42
4	3.14	0.14	3 00	0 42
5	2.68	0.24	2.83	0 25
6	3 39	0.22	2.73	0 22
Sum.....	18.76		17.72	
A.M.....	3.13		2 95	

* A.M. = arithmetic mean.

† S.D. = standard deviation.

Series II

This series consisted of six experiments, using T₁ as a single-tube cell. The technic followed was the same as in series I, velocities being observed at the depth where there was no movement of the liquid, i.e., where

$$r = \pm \frac{R}{2} \sqrt{2}$$

In the first two experiments of the series, half of the observations were made at the upper level, and half at the lower. In experiments 3, 4, 5, and 6, values were obtained at the upper level only.

Experimental results of series I and II are given in table 1.

Series III

Each of the three experiments in this series consisted of observations taken at levels differing by $50\ \mu$ throughout the depth of the cell, from ten to forty observations being taken at each level. From these observations the arithmetic mean of mobilities for each level was calculated. The mobilities at different levels plotted against depth resulted in curves of parabolic form; the mean mobilities of the maxima of these curves, obtained where $r = 0$, were 6.53 , 6.24 , and $5.61\ \mu$ per second per volt per centimeter, respectively, giving a mean mobility for the three experiments of approximately $6.1\ \mu$ per second per volt per centimeter. At the walls of the tubes the particles moved in the opposite direction, the mean mobilities for the three experiments giving values of -2.66 and $-3.10\ \mu$ per second per volt per centimeter at depths of $+R$ and $-R$ respectively.

TABLE 2

Electrophoretic mobilities of quartz particles in distilled water at 25°C., as determined in a single-tube cell from observations obtained at various levels in the cell

EXPT NO	MOBILITY IN μ /SEC /VOLT/CM.
1	2 37
2	2 16
3	2 13
Sum	6 66
A.M.	2 22

Electrophoretic velocity is given by equation 7. A rough approximation of this velocity is given by

$$U = \frac{2}{R^2} \sum_{r=0}^{r=R} V_{\text{obsd.}} \cdot r \, dr$$

This approximation is readily seen to be inaccurate unless observations are taken at a large number of levels, since it gives no weight to the value of the velocity at the axis of the tube, where $r = 0$, and gives undue emphasis to the value at the wall of the tube, where $r = R$. A better method of approximation consists in the use of the average of the mobilities observed at depths differing by dr . Values of mobilities so calculated for the three experiments in this series are given in table 2.

DISCUSSION OF RESULTS

Examination of the data in table 1 indicates that practically the same values of mobilities are given in the two cells. The value of the arithmetic

mean of the mean mobilities for the six series of experiments of series I is 3.13μ per second per volt per centimeter with a standard deviation of $\pm 0.31 \mu$ per second per volt per centimeter, and for the six experiments of series II, $2.95 \pm 0.31 \mu$ per second per volt per centimeter; hence there is no significant difference in the mobilities, as found in the two cells, greater than that which might be expected from the amount of variation in the experiments comprising a series. The mobility of quartz particles in triply distilled water at 25°C . as obtained by these two methods is therefore approximately 3.0μ per second per volt per centimeter.

The electrosmotic velocity of the liquid is equal to the difference between the electrophoretic velocity of the particles and the maximum observed velocity of the particles in the single tube (see equation 8); therefore the electrosmotic velocity of the liquid in the present case is $3.0 - 6.1$ or -3.1μ per second per volt per centimeter. With consideration of the relatively high experimental error inherent in experiments of the type concerned, these results seem to substantiate the theory that the electrophoretic mobility of the particles is equal in magnitude to the electrosmotic mobility of the liquid.

Comparison of mobilities given in table 2 with those given in table 1 shows that mobilities as obtained in the single-tube cell by means of observations taken at various levels in the cell are not equal, within the experimental error, to those obtained in the new cell or in the single-tube cell at depths of $\pm R\sqrt{2}/2$.

A plausible explanation of the different results obtained with the third method would seem to be that values not conforming to the theoretical values are obtained near the walls of the tube. Evidence in direct support of this is disclosed by examination of the data obtained in the three series of experiments. Since the electrosmotic mobility and the electrophoretic mobility appear to be equal in magnitude but opposite in direction, we should expect that there would be no movement of the particles at the wall of the tube. Experimentally, however, the particles at the walls were observed to move in the opposite direction from those at the axis of the tube. On the basis that the velocities should have been zero at the walls of the tube, the experimental values there determined were neglected, and the curves drawn to meet the axis, giving $V_{\text{obsd.}} = 0$ at distances $r = +R$ and $-R$, respectively. By interpolation of the values obtained at distances of 50μ from the walls, and use of the values as obtained experimentally at the other depths, approximation of mobilities by the method previously employed gave values of 2.87 , 2.93 , and 3.03μ per second per volt per centimeter, respectively, for the three experiments. These values are in the range of mobilities as obtained by the other two methods. This method of calculation of mobilities is not to be recommended for general use, however; it depends on the assumption that the electrophoretic mobility

of the particles is equal to the electrosmotic mobility of the liquid, a condition which would be expected to occur only in cases where the wall of the tube and the particles are of the same material, and has not been found to occur in all of these cases. Moreover, the method of interpolation does not give accurate results, since it is not known how far the influence of the wall extends. Another objection to the method lies in the large number of observations which must be made to obtain an approximation of the desired accuracy.

The advantages of the new cell in comparison with the single-tube cell, in both cases observations being made at the depths where theoretically there is no movement of the liquid, are apparent from a consideration of the values of standard deviations obtained in the experiments of series I and II; these are given in columns 3 and 5 of table 1. Standard deviation is an index of variance, i.e., it indicates how closely the values obtained are grouped about the arithmetic mean. The standard deviations found for the first two experiments in series II, in which values were observed at both the upper and lower levels in the single-tube cell, are much greater than the values of standard deviations obtained with the new cell. These high values probably came from failure to focus on the correct levels; it is difficult to find the correct levels such that readings at the upper and lower depths agree. It is also difficult to obtain readings at the lower level, therefore readings in the other four experiments of the series were taken at the upper level only. In all cases the microscope was refocused after each set of twenty readings. The values of standard deviations in experiments 3 and 4 of series II are also higher than those for the new cell, probably owing to the readings having been obtained at slightly different levels. In the last two experiments of this series standard deviations are not greater than with the new cell, indicating that observations were made at approximately the same level throughout the experiment; however, since these observations were made only at the upper level, it is difficult to be sure that the correct level was used. The uniformity of the values of standard deviations obtained in the experiments with the new cell (series I) make its advantages apparent. The correct level for observation is obtained readily; moreover, small differences in levels of observation do not introduce large errors in the observed values. For results of a certain degree of accuracy a smaller number of observations is justifiable with the new cell than with a single tube cell.

CONCLUSIONS

1. Values of electrophoretic mobilities of finely ground quartz particles in triply distilled water obtained in the new double-tube cell agreed within the experimental error with values as determined in a single cylindrical tube, in both cases observations being made at depths where theoretically there should be no movement of the liquid.

2. Values of electrosmotic mobilities obtained with a single cylindrical tube from observations made at various levels in the cell did not agree with values as obtained by the other two methods. Experimental evidence suggests that erroneous values are obtained in the walls of the tube.

3. The approximate electrophoretic mobility of quartz particles in triply distilled water as obtained by the two methods which agreed within experimental error was 3.0μ per second per volt per centimeter.

4. The value of electrosmotic mobility of water in quartz tubes as obtained from these experiments was approximately -3.1μ per second per volt per centimeter.

5. Consistency of experimental results with the new double-tube cell indicates the advantages of the new cell.

REFERENCES

- (1) ABRAMSON, H. A.: *Electrokinetic Phenomena*. The Chemical Catalog Co., Inc., New York (1934).
- (2) LAMB, H.: *Hydrodynamics*, 6th edition. Cambridge University Press, London (1932).
- (3) NORTROP, J. H.: *J. Gen. Physiol.* **4**, 629 (1922).

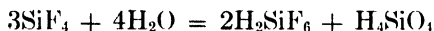
SILICA FLUFF

C. A. JACOBSON

*Industrial Science Division, Department of Chemistry, West Virginia University,
Morgantown, West Virginia*

Received September 18, 1935

A form of hydrated silica is obtained by drying at a low temperature the silicic acid resulting from the action of silicon tetrafluoride upon water. This product possesses unusual properties, and has been called silica fluff to distinguish it from all other forms of silica. The reaction is formulated as follows:



When silicic acid precipitates from water solution it is a transparent gel, growing gradually translucent and opaque when filtered and dried. If left for some weeks drying in the open air it assumes the above-mentioned white fluffy character. No apparent change takes place in the material after a month's drying, and it maintains its composition over a period of years as definitely as does quartz itself.

This light, fluffy, white powder is composed of aggregates of tiny flakes of irregular outline, containing inclusions of air bubbles of uniform size that give color phenomena with polarized light, as if the substance were composed of doubly refracting globular crystals. These tiny air inclusions cannot be observed except with a 600 diameter magnification, or larger.

The specific gravity of the material is 1.018, as determined by obtaining the volume of kerosene displaced by a given weight of silica fluff, using an oil pump to remove the air from the pores of the material. The specific gravity of orthosilicic acid is 1.57, and for the meta acid 2.2, while the specific gravity of anhydrous silicon dioxide varies from 2.3 to 2.6. It is apparent, therefore, that the low specific gravity of silica fluff, a lower hydrated form of silica than metasilicic acid, is due to the air inclusions in the flakes which cannot be dislocated by a vacuum pump.

Weighed in air, under as nearly the same degree of packing as possible, the apparent specific gravities of a number of light materials in comparison with silica fluff are given in table 1. It is seen that even ground cork and air-floated carbon black are more than twice as heavy as silica fluff. Numerous attempts have been made to duplicate this material, but no other product has been quite so light or with as high air adsorption as the mate-

rial which the author made at the Johns Hopkins University in 1919-20. The long time required for drying, as well as the high humidity during the drying, may account for these unusual properties.

Silica fluff has an index of refraction of 1.45. The flakes are from 0.01 to 0.3 mm. in diameter and from 0.003 to 0.008 mm. in thickness. The diameter of the air bubbles is 1.0 to 1.5 microns.

TABLE 1

Apparent specific gravity of silica fluff compared with that of other light materials

MATERIAL	SPECIFIC GRAVITY
Silica fluff	0.0218
Ground cork	0.0621
Carbon black (high color gas carbon)	0.0635
Swedish soft wood flour	0.1543
Silica black, Grade A	0.2201
Merck's precipitated silica	0.2265
Lycopodium powder	0.3624
Powdered silica	0.9199

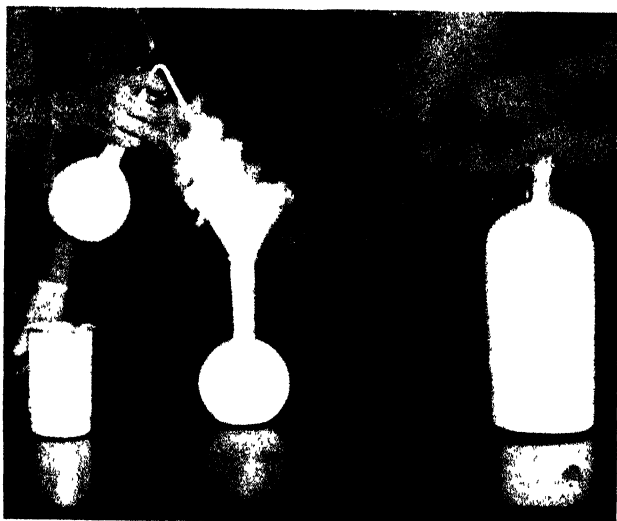


FIG. 1. Silica fluff

On account of its high air adsorption silica fluff behaves like a liquid, flopping and splashing from side to side in the bottle, and can be poured through a narrow-stem funnel or blown through a wash bottle like a liquid, as is shown in figure 1.

No elements were found to be present in silica fluff other than silicon,

hydrogen, and oxygen, but the last two are not in the ratio to form water. Its composition is given in table 2. From the percentage composition obtained by experiment its empirical formula is calculated to be $H_6Si_{12}O_{27}$ or $(SiO_2)_{12} \cdot 3H_2O$. A survey of the literature brings out the fact that Victor Lenher (5) reported silicic acid desiccated over concentrated sulfuric

TABLE 2
Analysis of silica fluff

LOT	H ₂ O AT 120°C.	H ₂ O AT BRIGHT CHERRY RED HEAT (800 - 850°C.)	TOTAL H ₂ O	SiO ₂ BY H ₂ F ₂
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
1	0.48	6.60	7.08	92.92
2	0.43	6.76	7.19	92.80
Average.....	0.455	6.68	7.135	92.865

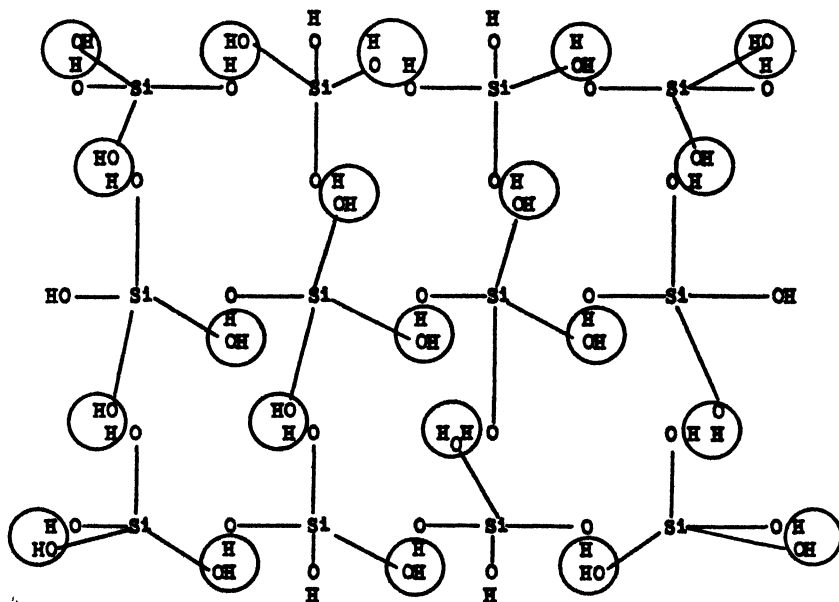
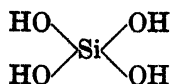


FIG. 2. The condensation of twelve molecules of orthosilicic acid, by elimination of twenty-one molecules of water, to yield silica fluff

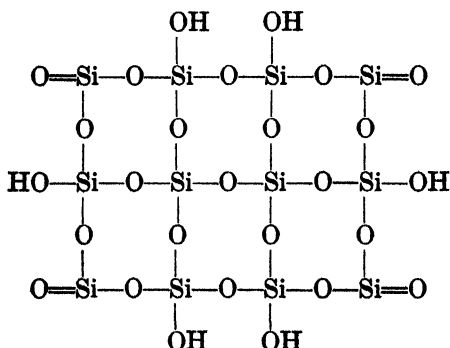
acid for two months with a water content of 6.75 per cent. G. Tschermak (8) obtained a similar product, also desiccated over sulfuric acid, with a water content of 6.7 per cent. Bernhard Neumann (7) investigated the dehydration of silicic acid from 200° to 1000°C., starting with a product having a water content of 6.6 per cent.

The above-mentioned analyses, together with those obtained in this laboratory, furnished the basis for the following speculation regarding the structure of the molecule of this very stable and remarkable form of silica or silicic acid.

Apparently there are three molecules of water in the compound. On the basis that dihydrated silicon dioxide is orthosilicic acid, in which the water is incorporated in four hydroxyl groups as seen in the graphic formula



the author was led to place twelve such molecules in juxtaposition and to eliminate twenty-one molecules of water where the hydroxyl groups are in proximity to each other (see figure 2), yielding a molecule which exactly fits the analysis, and is represented by the following graphic formula for silica fluff.



A compound with this formula calls for a molecular weight of 774.77, of which 6.98 per cent is water, whereas the average water content obtained experimentally is 7.13 per cent.

If we consider that some of the water obtained at 120°C. existed free, the hydroxyl groups in the formula exactly represent the water obtained when the material was ignited.

Assuming that dehydrated silicic acids possess structures of this type it is easy to understand how various degrees of hydration can be had, and consequently how dehydration may take place so gradually that no noticeable break in the curve appears. If we assume, for example, that the four corner silicon atoms in the graphic formula hold eight hydroxyl groups instead of four oxygen atoms, the water content will amount to 14.89 per cent.

Many workers in this field, for example, O. Mugge (6), H. Chatelier (3),

J. Bruckmoser (1), G. Tschermak (9), H. Kantsky (4), and others, have expressed varied opinions about the composition of silicic acids and the nature of the water which they contain.

It is a well-known fact that diatomite, more often called diatomaceous earth or kieselguhr, is almost wholly siliceous (85 to 92 per cent silica). This material has resulted from the accumulation of the remains of unicellular organisms called diatoms, whose living structure must have contained silica in some soluble form.

Now upon the decomposition and dehydration of this siliceous material it might be expected that a product would result, similar in properties to silica fluff, especially in its relation to combined water.

To test this theory, the water contents of various diatomaceous earths are given in table 3. All but one of these values are taken from analyses reported by Calvert (2). The percentages in the table are based upon the total weight of the diatomaceous earth samples and not upon the silica

TABLE 3
Water content of diatomaceous earths

SOURCE	WATER CONTENT	SOURCE	WATER CONTENT
	<i>per cent</i>		<i>per cent</i>
Herkimer, N. Y.....	12.12	Monterey, Calif.....	4.89
Richmond, Va.....	8.37	Toome, Ireland	7.35
Wilmington Wharf, Va.....	3.40	Algiers...	9.14
Pope's Creek, Md.....	3.47	Algiers...	3.50
Ellensburg, Wash.....	5.98	Algiers.	7.40
Fossil Hill, Nev.....	5.99	Storey County, Nev.. . . .	6.07
Lompoc, Calif.....	5.00		
Average of all values.....			6.36

present in them. When these percentages are recalculated on the silica content alone, excluding the sample from Herkimer, N. Y. (which obviously contains adsorbed water), the average per cent of water in the silica of twelve different samples of diatomaceous earth becomes 7.15, which is almost identical with the water normally present in silica fluff, whose molecular structure is postulated in the graphic formula shown.

This fact would seem to be more than an accidental coincidence. The combined water in diatomaceous earth cannot be present in the form of definite hydrates, for no sharp break in the dehydration curve has ever been reported. It would not be surprising, however, if the silica and combined water in diatomaceous earth exist in some such way as that postulated for silica fluff.

REFERENCES

- (1) BRUCKMOSER, J.: Sitzber. Akad. Wiss. Wien **118**, 1635.
- (2) CALVERT, ROBERT: Diatomaceous Earth. The Chemical Catalog Co., Inc., New York (1930).
- (3) CHATELIER, H.: Compt. rend. **147**, 660 (1908).
- (4) KANTSKY, H.: Z. anorg. Chem. **117**, 209-42 (1921).
- (5) LENHER, VICTOR: J. Am. Chem. Soc. **43**, 391 (1921).
- (6) MUGGE, O.: Centr. Mineral. Geol. **1908**, 1928-34.
- (7) NEUMANN, BERNHARD: Z. angew. Chem. **43**, 882 (1930).
- (8) TSCHERMAK, G.: Z. anorg. Chem. **63**, 230-74 (1909).
- (9) TSCHERMAK, G.: Z. anorg. Chem. **87**, 300 (1914).

ADSORPTION OF RADON BY GLASS

S. C. LIND AND ROBERT LIVINGSTON

School of Chemistry, University of Minnesota, Minneapolis, Minnesota

Received September 18, 1935

During the course of certain radiochemical experiments it was noticed that radon which was kept for several days in Pyrex bulbs was in part strongly adsorbed on the glass (1). The bulbs were thin walled, and had volumes of approximately 0.1 cc. The pressure of the impurities which accompanied the radon was never greater than a few millimeters, and was probably in most cases less than 1 millimeter. The bulbs were blown from clean tubing, but were not subjected to any chemical cleaning after being made. The sealed bulbs containing the radon were introduced into a horizontal tube which was attached by 20 cm. of 2-mm. capillary tubing

TABLE 1

Evidence for the slow irreversible adsorption of radon on glass

INITIAL AMOUNT OF RADON IN MILLICURIES	TIME DURING WHICH THE RADON WAS SEALED IN THE BULB	PER CENT OF THE RADON WHICH REMAINED ON THE WALLS OF THE BULB
<i>mc.</i>	<i>hours</i>	<i>per cent</i>
156.5	17.5	<1
188.5	37	11
119.7	49	19
102.5	68	16

to a 100-cc. vessel. After the system had been evacuated (to a pressure of less than 10^{-4} mm.), it was cut off from the vacuum line, and the 100-cc. vessel was immersed in liquid air. The fragile bulb containing the radon was then shattered by a magnetically-operated, glass-enclosed plunger. The distribution of the fluorescent glow indicated that the greater part of the radon distilled over almost instantaneously. After fifteen or twenty minutes the side tube was sealed off from the 100-cc. vessel, which was still immersed in liquid air. Six or eight hours later the side tube was examined in the dark. If the glass showed any fluorescence, the amount of radon was determined (usually twenty or thirty hours after breaking the bulb) with a γ -ray electroscope. It is noteworthy that in every case where radon remained in the tube, the fluorescent glow was visible only on the fragments of the bulb. Even after forty hours there

was no visible evidence that any of the radon had diffused into the containing tube. Table 1 summarizes the available quantitative evidence.

Although it is not precluded that the observed differences in the percentage adsorption may be due to possible differences in the surface of the bulbs or in the impurities of the radon, these data suggest that the percentage adsorption depends upon the time of contact. It is possible that the adsorption may be the result of "pitting" of the glass by α -particle bombardment. In this case the adsorption would be proportional to the intensity of the α -particle bombardment on the glass. These results make it obvious that certain precautions must be taken in the transfer or measurement of radon used in radiochemical experiments; particularly is it undesirable to leave radon in a small tube longer than necessary for the gamma-ray measurement before transferring it.

REFERENCE

- (1) LIVINGSTON AND REYERSON: J. Phys. Chem. **37**, 534 (1933).

NEW BOOKS

Origins and Development of Applied Chemistry. By J. R. PARTINGTON. 25 x 15 cm.; xii + 597 pp. London: Longmans, Green and Co., 1935. Price: 45s. net.

Dr. Partington's book arrived as the reviewer was leaving for the United States, and the "Origins" became his constant companion in America. The reviewer had full opportunity for reading the work most thoroughly. Dr. Partington's book, by its encyclopaedic knowledge, seems at first perhaps a little frightening, but as the study of the book proceeds so one's admiration for it grows. This is not just a reference book. It is much more than that, and a careful reading through the whole work as it stands would fully repay the time and energy devoted to it.

No single reviewer can really do justice to the "Origins," in view of its tremendous scope and the comprehensive nature of its information. The writer has therefore judged the book solely from its plant chemical content, with which he is familiar. Students of the history of plant chemistry will find a great deal of information on the plant materials of Egypt, Babylonia and Assyria, Crete, Troy and Cyprus, Asia Minor, Persia, Phoenicia, and Palestine. The information contained on these lines has taught the reviewer to appreciate not only the extent but also the soundness of Dr. Partington's knowledge. A survey of the plant materials contained in this book revealed nothing that is not mentioned in it, and some of the most difficult points on the history of plant chemistry have been dealt with in a manner that commands only admiration. To take one example (p. 169), the case of kyphi, the incense of the Egyptians: this is a most difficult topic, and Professor Partington has threaded through it with care and remarkable lucidity. Kyphi has been the object of many lengthy discussions, and Dr. Partington has managed to convey all that is known about it without leaving that peculiar feeling of uncertainty one has after the study of this subject in other works. Those who know the difficulties must appreciate Dr. Partington's attitude, and those who are blessedly ignorant of them do not realize through what a maze they have been so successfully conveyed,—a most remarkable achievement. Attention must also be drawn to the helpful indexes, especially the subject index, which contains many references to plants and plant materials.

Viewed from any aspect, there is no doubt that Dr. Partington's "Origins" will become one of the classics on the history of chemistry.

M. NIERENSTEIN.

Electron Emission and Adsorption Phenomena. By J. H. DE BOER. The Cambridge series of physical chemistry. Translated from the manuscript by Mrs. H. E. Teves-Acly. 398 pp.; 150 figs. The Macmillan Co., The University Press at Cambridge, England, 1935.

The author deals with the nature of surface forces as revealed by the study of electron emission from metals and dielectrics and by the knowledge of adsorption of substances on such surfaces. He hopes to obtain information on the subject of adsorption on surfaces by studying their electron emission, and, vice versa, he expects to learn concerning the nature of electron emission by a study of adsorption phenomena on surfaces. From the nature of these topics it is at once seen that the book is of interest to individuals who are concerned with the nature of catalysis. Since this latter phenomenon is of the greatest importance to chemists, the book should appeal

to a large circle of readers. The subject-matter of the volume does not include the phenomena of catalysis however. Indeed the word "catalysis" is not found in the index! It is merely the reviewer's opinion that the studies portrayed here should be of interest to physical chemists who wish to elucidate the problems of catalysis. The methods of research employed and discussed by the author may well find extended application and lead to a richer and more precise knowledge of surface chemistry. The content of this interesting book is divided into fifteen chapters and can be discussed in the briefest manner by mentioning the various topics: electron emission from metals; the nature of adsorption forces; the adsorption of cesium on tungsten surfaces and other electropositive metals on metal surfaces; photoelectric emission after adsorption of electropositive metals on metal surfaces; double layers formed by the adsorption of gases; the adsorption of light by matter in the gaseous and in the adsorbed state; the selective photoelectric effect; alkali-metal atoms adsorbed within the lattice of the alkali halides and their photoelectric properties; electronic conduction in the lattices of the alkali halides and other lattices; photoelectric cathodes with thick intermediate layers of a dielectric and metal particles; thermionic emission of cathodes with a dielectric; oxide-covered cathodes; emission of electrons into intermediate layers of dielectrics and into blocking layers. The author makes abundant use of energy diagrams in his discussion. To the chemist with modern training this method of treatment should be very satisfactory.

GEO. GLOCKLER.

The Structure of Crystals. Supplement for 1930-34 to the second edition. By RALPH W. G. WYCKOFF. American Chemical Society Monograph No. 19A. 240 pp.; 75 figs. New York: Reinhold Publishing Corporation, 1935.

The present volume supplements the second edition of the author's well-known treatise and covers the work for the last four years on structure determination of crystals by x-ray methods. The eleven chapters are numbered to correspond to those in the second edition, and an appendix gives the complete literature of the subject. The same chronological arrangement is maintained as is found in the second edition. This bibliography covers sixty-one pages. It is evident that the book is indispensable to the worker in the field of crystal structure determination, but any one interested in the general field of atomic and molecular structure and the solid state will by necessity have to refer to this treatise-supplement. The figures shown are excellent in execution and an invaluable help in understanding the intricate patterns of the more complex crystals. The book represents an enormous amount of the most painstaking effort, and the author is to be congratulated on the result of his labors.

GEO. GLOCKLER.

Body Water—The Exchange of Fluids in Man. By JOHN P. PETERS. 14.5 x 23 cm.; 5 figs.; viii + 405 pp. Springfield, Illinois, and Baltimore, Maryland: Charles C. Thomas. Price: \$4.00.

There has been great need for such a comprehensive discussion of the rôle of water in the vital processes of the human organism. Professor Peters is excellently qualified to bring together the many papers which have been published in this field and to discuss them critically, inasmuch as he has himself actively worked in this field for many years.

This volume contains much more than its title would indicate. In addition to considering the composition of the various body fluids, it is a rather complete survey of the physiology of the absorption, secretion, and excretion of many substances such as carbohydrates, nitrogen-containing compounds, fats, salts, etc., within the

body, all considered in the light of the direction of water flow which takes place either through interstitial spaces or across membranes.

The maintenance of equilibria between various fluids and tissues by means of the Gibbs-Donnan phenomena, osmotic pressure, "colloid osmotic pressure," tissue tension, etc., are adequately discussed from the standpoint of both theory and application, and the effect of these forces in causing fluid flow, ultrafiltration, and absorption is emphasized. Both normal and pathological physiology are considered.

Every chapter contains applications of physicochemical principles to physiological processes, so that the book would serve admirably as reference and source material for courses in physical chemistry designed to emphasize physiological and medical aspects.

The reviewer was particularly desirous of seeing how the question of "bound water" would be treated. To his surprise it was rather summarily dismissed without any particular discussion, the author believing that bound water does not exist as a measurable entity. Similarly the imbibition pressure of colloids is spoken of (p. 53) as if it were of no particular significance.

In a discussion of the exchange of fluids between blood cells and serum the author considers (pp. 120-3) that the "potassium salts of hemoglobin" are largely "undissociated." This view is decidedly at variance with those of certain physical chemists who have assumed a stoichiometrical compound formation between proteins and acids and bases, with a subsequent complete ionization of the "salt." It is difficult for the reviewer to see how a potassium-protein "salt" can be completely or nearly completely unionized, whereas adsorption of potassium on the protein micelles would account for such behavior.

The chapter headings are as follows: (1) Chemical forces which control exchanges of fluid and solutes; (2) The nature and movements of interstitial fluid and lymph; (3) Exchanges between blood and interstitial fluids; (4) Serous fluids and transudates; (5) Exchanges between blood cells and serum; (6) Exchanges between tissue cells and interstitial fluids; (7) Water of oxidation and the losses of water and solutes through skin and respiratory passages; (8) Alimentary exchanges; (9) The general nature of renal activity; (10) Renal excretion of filtrable organic solutes; (11) Renal excretion of water and inorganic salts; (12) Nervous and hormonal control of urine excretion.

The author lists complete titles and journal citations to 875 references in the author index and also indicates the specific pages in the text where the reference is considered. A short but adequate subject index closes the volume. The volume should be carefully read by all students of physiological processes.

ROSS AIKEN GORTNER.

Monographien aus dem Gesamtgebiete der Mikrochemie. Farbmessungen, Theoretische Grundlagen und Anwendungen. By E. HASCHKE and MAX HAITINGER. 85 pp.; 6 figs.; 14 tables. Wien and Leipzig: Emil Haim and Company, 1936.

Although the sensation of color is entirely subjective, it is possible to measure the qualities responsible for the sensation in a more or less exact way. In doing so the description of color becomes independent of subjective impressions and external conditions. The quantitative measurement of color has been codified by international agreement some years ago. Based on the color theory of Young-Helmholtz, which distinguishes between hue, saturation, and brightness as the characteristics of color, the authors derive the quantitative expression of these magnitudes. The monograph is of interest not only to chemists and physicists but to anyone interested in the quantitative description of color. Contrary to the authors, the reviewer is of the opinion that in the characterization of a certain object the quantitative

description of color is of secondary significance only, since the color is a function of the state of subdivision of the object. It seems, therefore, an exaggeration to state (p. 57): "Der Farbpunkt spielt eine ähnliche Rolle wie der Schmelzpunkt oder Siedepunkt."

I. M. KOLTHOFF.

Structure and Properties of Matter. By HERMAN T. BRISCOE. 420 pp. New York: McGraw-Hill Book Company, 1935.

The author states that his object is to present to students of chemistry a readily understandable account of the newer discoveries in the physical sciences which have brought about the great advances since 1900 in our knowledge of the nature of matter. The book is addressed not to specialists but to those having sufficient training,—presumably this might mean Senior or possibly Junior Chemists, or graduate students in chemistry not majoring in physical chemistry.

The reviewer is quite in sympathy with the desirability of such a course, and believes that the author has furnished a very acceptable text for the purpose in mind. Among other subjects he treats the electron, the proton, the nucleus, radioactivity, crystal structure, radiation as introductory to Bohr theory, valence, and quantum mechanics.

Some of the minor defects can easily be remedied in a future edition, such as revision of the list of isotopes on page 115, the substitution of the modern values of atomic weights in the actinium series (page 67), and the use of the older assumption that there are free electrons in the nucleus. Probably geophysicists and cosmic physicists would not agree that any extensive formation of new nuclei has occurred on our planet, though this is an interesting field for speculation.

While some of the material presented may be included in other courses in general and physical chemistry, the present book meets a real need for the advanced undergraduate in chemistry who does not intend to specialize in some phase of atomistics.

S. C. LIND.

Die Bierhefe als Heil-, Nähr-, und Futtermittel. By JULIUS SCHÜLEIN. (Technische Fortschrittsberichte. Fortschritte der chem. Technologie in Einzeldarstellungen. Herausgegeben von Prof. Dr. B. Rassow, Leipzig.) 22 x 15 cm.; vi and 194 pp. Dresden und Leipzig: Theodor Steinkopff, 1935. Price: geheftet, 9RM; gebunden, 10RM.

This book deals with brewer's yeast as an aid to nutrition and pharmacology. The therapeutic value of yeast is taken to depend largely on its vitamin content, and much of the book is devoted to an account of the vitamins so far as they occur in yeast or can be invoked therein by irradiation. The author includes much of the most recent work, but shows a lamentable lack of first-hand acquaintance with the English literature on the subject. No reference appears to be made to the important work of the International Committee on Vitamin Standards. A detailed account, supported by references to the medical literature, is given of the application of yeast and yeast preparations to the cure of a large number of diseases.

The value of yeast as a nutrient also depends in a large measure on its vitamin content, but in addition the protein, salts, and other constituents are in themselves of great nutritive value. Dried yeast is advocated as an addition to the normal diet of human beings on the ground, no doubt valid in many districts, that at the present time the ordinary diet of large numbers of people does not contain sufficient of the various vitamins to ensure complete health and resistance to disease.

In the field of animal nutrition yeast may also play an important part, and striking results are quoted with respect to the increased milk production of cows fed on a diet containing irradiated yeast.

The author has brought together in this work an imposing mass of material showing in how many ways yeast can be usefully employed dietetically, and although it is obvious that he is putting forward the best possible case for the use of yeast, there seems to be no doubt that there is a large nutritional field in which yeast may be usefully employed.

A. HARDEN.

The Structure of Metallic Coatings. A General Discussion held by the Faraday Society. 25 x 16 cm.; 247 pp.; 77 plates. London: Gurney and Jackson, 1935. Price: 21/- net.

This volume has been reprinted from the Transactions of the Faraday Society and is divided into the two main sections "Electron Diffraction Methods" and "The Structure of Metallic Coatings," each followed by discussion on the individual papers. Professor Desch contributes an introductory paper, and various aspects of the electron diffraction method of examining surface structure are discussed by G. P. Thomson, G. I. Finch, W. E. Laschkarew, H. G. Hopkins, and others. The most interesting paper in part I is certainly that of Finch and collaborators; in this the problems of electron diffraction and surface structure are dealt with very thoroughly. A very interesting point concerns the appearance of "extra" rings not normally associated with the particular solid. Finch has shown that they are due to the entry of gas into the crystal lattice. The hope of many, that electron diffraction would play an important part in the solution of problems of gas absorption in metals, appears likely to be fulfilled in the near future.

The second part of the discussion is perhaps not quite so well arranged as it might be; the papers dealing with x-ray work would have fitted better into the physical scheme of part I. The papers in this section are too numerous to receive detailed individual attention. A considerable section deals with the properties and structure of electrodeposited layers. Andrade deals with the crystallization of thin metal films, Ornstein with optical research on evaporated metal layers. Both the authors represented in this volume and their publishers are to be congratulated on the particularly fine set of plates collected here.

J. T. RANDALL.

The Eruption of Mt. Pelee, 1929-32. By FRANK A. PERRET. Publication No. 458 of the Carnegie Institution of Washington, 1935. 9 x 11.5 in.; 126 pp.; 71 figs., 3 diagrams and a chart of *nuée ardente* activity; 2 appendices.

The investigation here reported was *lived* on the mountain itself, day and night. Excursion, observation, photography, and intermittent sleep were the author's lot.

The report opens with a brief discussion of terminology, and a history of Mt. Pelee, which has erupted before. The main part of the book is in two parts,—first a narrative of the eruption of 1929 to 1932, and then an analytical study of the volcanic activity. Chemical studies include only an analysis of water in the first appendix, but the lack is not so serious because the lavas are surprisingly similar to those of the 1902 eruption, well studied by Lacroix. The emphasis here is on the physical aspects.

Volcanic flows differ in their physical condition: first, the Mauna Loa type of swiftly moving, luminous, coherent liquid; second, the Etna type, more viscous, consolidating at the surface into discrete blocks; and third, the Pelean type with its autoexplosive liquid, self-expelled in the form of a completely subdivided mass of still active particles isolated from one another by vapor films—the whole mass flowing down any slope with incredible speed because it is frictionless. The particles of liquid lava contain vapors in solution and give them off so rapidly that they are cushioned from each other, and the great avalanches rush down the mountain slopes in utter silence! These are the *nuées ardentes* named in reference to the clouds

which rise, but the name does not adequately express the great source of energy in the avalanche at the base of the cloud.

The data are microphonic, seismologic, and astronomic, in addition to the narrative of major events and a few notes on the temperatures. The observed speeds of flow of the *nubes ardenites* ranged from 10 to 33 meters per second. There are some electrical charges from the clouds, and "flashing arcs" are described as possibly light reflected from a sound wave-front.

One physicochemical hypothesis is presented by the author with the frank remark that it may be "outrageous,"—namely, that at depths some igneous magma may be in a vapor phase because of excess heat. The latest statement of expert opinion on this is by Fenner (in *Economic Geology*, volume 30, pp. 929–930, 1935) and is unfavorable to the idea, showing also that high pressures may develop from dissolved gases without having the magma itself become gaseous.

The general reader will find interest in the section (pp. 8 to 12) on the diagnosis and prediction of volcanic eruption, and in the many excellent photographs.

FRANK F. GROUT.

Das Kristallzeichnen auf Grundlage der stereographischen Projektion. By H. TERTSCH. 28 x 15 cm.; iv and 38 pp.; 34 figs. Wien: Julius Springer, 1935. Price: 3.60 RM.

The orthodox methods of drawing crystals from a stereographic projection are described with special emphasis on their application to the study of habit. Successive sections deal with the drawing of a plan on the plane of projection and with representation in parallel perspective on an arbitrary plane, the true habit being obtained by the use of measured central distances. A further section describes the drawing of twin crystals. The writing is clear and concise, but a few of the more complicated figures might have been reproduced with advantage on a larger scale.

F. C. PHILLIPS.

Wasserstoff-Ionenkonzentration (pH). By H. JÖRGENSEN, with an introduction by S. P. L. Sörensen. 15 x 22 cm.; 264 pp. Dresden: Theodor Steinkopff. Price: paper, 15 RM; bound, 16 RM.

In recent years there have appeared both in the English and in the German languages, a number of excellent books dealing with the determination and applications of hydrogen-ion concentrations; the author of the book under review has nevertheless written another, apparently at the request of the publishers to fill a gap in their series of scientific monographs. Nearly half of the book, 114 out of 246 pages of text, is devoted to a consideration of the fundamental principles involved in the determination of pH, and the theoretical aspects of electrode potentials, buffer solutions, and electrolytic equilibria are discussed in a concise but adequate manner. The treatment of acids and bases is particularly interesting, since the author adopts throughout the modern viewpoint which regards acids as yielding and bases as accepting protons, respectively.

The next section of the book, 52 pages in length, consists of a review of the methods of measuring pH; the author does not intend this to be complete, for the reader is referred to other treatises for further practical details. Nevertheless the methods of using the hydrogen and quinhydrone electrodes are described in sufficient detail, but the account of the glass electrode is little more than an indication of how it can be used. Colorimetric methods for determining pH, which either do or do not involve the use of buffer solutions, are described, although the simple "drop-ratio" method of Gillespie is not mentioned.

The last portion of the text, entitled "Technischer Teil," occupies some seventy pages, and in it are described sixty-two examples of the importance of measurements

of hydrogen-ion concentrations in industry: amongst these are references to fermentation, baking, sugar, paper, leather, organotherapy, agriculture, milk, confectionery, textiles, and dyeing. A ten-page appendix on the subject of pH in acid-alkali titrations then follows, and it is here that the newer concept of acids and bases is particularly useful. The book is completed by a list of over two hundred and forty references, arranged in alphabetical order according to the names of the authors, and there is also a good subject index. It is not surprising to find a relatively large number of references to Danish and Scandinavian literature, since the author is working in Copenhagen, but English, American, and German journals are well represented in the list. The book can be recommended as giving an excellent survey of the subject of hydrogen-ion concentrations; its viewpoint is up to date and it is written in a clear and simple style.

S. GLASSTONE.

Journal of the Institute of Metals. Volume LVI (Proceedings), No. 1, 1935. 306 pp.; 31 plates. Cloth. Edited by G. Shaw Scott, M.Sc., F.C.I.S. London: The Institute of Metals, 36 Victoria Street, Westminster, S.W.1. Price: £1. 11s. 6d.

The latest volume of the *Journal of the Institute of Metals*, Volume LVI, No. 1, 1935, constitutes a complete record of the two most recent meetings of the scientific society that is responsible for the publication of this useful book. The respective gatherings were the Spring Meeting and the May Meeting, both held in London. At the latter Professor W. L. Bragg, F.R.S., delivered the twenty-fifth annual May Lecture, his subject being "Atomic Arrangement in Metals and Alloys." This discourse—in which an account of the theory of atomic arrangement in the crystalline structure of an alloy is given—is reproduced in full, and constitutes a valuable addition to scientific knowledge. It brings up-to-date the work that has been done on this subject since Professor Bragg's father, Sir William Bragg, F.R.S., delivered a previous May Lecture—in 1916—on "X-rays and Crystalline Structure, with Special Reference to Certain Metals."

A dozen papers dealing with many aspects of metallurgical work make up the bulk of the present volume, these papers having been presented at the March Meeting of the Institute of Metals. Two specially interesting groups are those dealing with fatigue in metals due either to atmospheric action or to corrosion. Another group is devoted to the constitution or properties of tin alloys. "Unsoundness in Aluminium Sand Castings" and "The Mechanical Properties of Some Wrought Magnesium Alloys" are the titles of two other papers of considerable industrial importance. All these and other papers, which are very fully illustrated—for the most part by photomicrographs—are reproduced *in extenso*, together with a record of the discussions which took place when they were presented and written communications upon them that have been subsequently made.

As the March Meeting was also the Annual General Meeting it is appropriate that in the present volume there should appear the Report of Council on the work of the Institute for the past year, the report showing that the work of the Institute has been fully maintained.

Metallurgical Abstracts (General and Non-ferrous). Volume I (New Series) 1934. 780 pp. Cloth. Edited by G. Shaw Scott, M.Sc., F.C.I.S. London: The Institute of Metals, 36 Victoria Street, Westminster, S.W.1. Subscription price: £4, inclusive of two "Proceedings" volumes.

Metallurgical Abstracts, published under this title since January 1931 and issued as a supplement to *The Monthly Journal of the Institute of Metals*, has appeared hitherto as part of the *Journal* series. The present issue of *Metallurgical Abstracts*

is the first volume of a new series; it appears in a distinctive binding and is complete with its own index containing many thousands of entries.

The extent of the publication can be gauged from the fact that the abstracts are gleaned from over one thousand of the world's scientific and technical publications by a staff of fifty-eight abstractors and reviewers whose names form an impressive list on the opening page of the new volume.

The subjects dealt with are grouped under twenty-four main headings and range from "Properties of Metals" to "Industrial Uses and Applications." It is difficult to overrate the value of these abstracts to the busy man who desires to keep in close and regular touch with important technical developments in various parts of the world.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System Nummer 4: Stickstoff. Lieferung 2. 26 x 18 cm.; pp. x + 283-506. Berlin: Verlag Chemie, 1935. Price: (abroad) 26.25 marks.

The second issue of the volume on nitrogen deals entirely with its compounds with hydrogen and the greater part is devoted to ammonia, including its manufacture. The discussion of synthetic ammonia includes the Haber, Claude, Casale, Fauser, and other processes. The text has been submitted in some cases to the technical interests, who are not likely to have disclosed much of value. The physical and chemical properties of ammonia are very fully dealt with and there are numerous tables and diagrams in the text. The literature references are brought to May, 1935, and in the section dealing with the manufacture of ammonia are less satisfactory than usual, reference to English publications being surprisingly incomplete.

J. R. PARTINGTON.

Eisen- und Stahllegierungen. Patentsammlung. 1. Ergänzungsheft. By A. GRÜTZNER. Zugleich Anhang zur Metallurgie des Eisens in Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. 26 x 18 cm.; 425 pp. Berlin: Verlag Chemie, 1935. Price: unbound, 44 marks; bound, 48 marks.

This volume is a supplement to that published by the same author and in the same series in 1932, and forms an independent supplement to Gmelin's *Handbuch*. It includes patents in Austria, England, France, Germany, Switzerland and the United States of America for the period from March 1932 to the end of 1934. It gives in three columns the composition, the properties and applications, and the patent references. The alloys are classified according to composition. Although the first part included patents from 1880 to 1932, it was a hundred pages smaller than this supplement, so that some idea may be gained of progress in recent years in this field of metallurgy. The work is likely to prove very useful in technical libraries.

J. R. PARTINGTON.

THE HEAT CAPACITY OF SATURATED SODIUM SULFATE SOLUTION

KENNETH A. KOBE AND CLARENCE H. ANDERSON

Department of Chemical Engineering, University of Washington, Seattle, Washington

Received October 17, 1935

The heat capacity of saturated sodium sulfate solution is of importance in the problem of recovery of the anhydrous salt from its aqueous solution. No data are reported in the literature for the saturated solution. In fact, data for heat capacities of practically all saturated solutions in contact with the salt are not in the literature.

APPARATUS

Heating element. A piece of Pyrex tubing, inside diameter 3 mm., is drawn out to give a thin-walled center section 1 meter long and 1 mm. in diameter. A 20-gauge copper wire is soldered to one end of a piece of 28-gauge constantan wire 1 meter long. The constantan wire is threaded through the tubing and the end soldered to another 20-gauge copper lead wire. The fine glass tubing is wound into a spiral approximately 35 mm. in diameter and with 3 mm. between the turns. The ends of the heavy tubing containing the copper leads are brought up at right angles to the plane of the spiral. The copper leads are connected to the lower ends of binding posts in a suitable cork stopper.

Calorimeter arrangement. A 200-cc. wide-mouth Dewar flask is used. In the cork containing the heating element are a 100°C. calibrated thermometer graduated in tenths and a glass drill stirring rod driven by a motor stirrer. The heating element is placed in a circuit with suitable variable resistances, calibrated ammeter, and voltmeter across the heating element to check constantly the resistance of the heating element.

Water equivalent. A constant current of 1 ampere is passed through the heating element immersed in 100 g. of water in the calorimeter. The range of temperature is 25° to 95°C. At each 10°C. interval the current is shut off and the rate of cooling determined. The room temperature is maintained constant.

HEAT CAPACITY, 32.4°C. TO 102.8°C.

Above the transition temperature of sodium sulfate decahydrate (32.4°C.) the solubility curve is inverted. A saturated solution of the

salt is prepared at 34.5°C. and 100 ml. of it is pipetted into the calorimeter. One gram of excess anhydrous salt is added to insure crystallization of salt from the solution as the temperature rises. Data are taken over the range 35° to 95°C., with cooling curves at 10°C. intervals, as in the determination of the water equivalent. One additional correction must be made in the

TABLE 1
Heat capacity of saturated sodium sulfate solution

TEMPERATURE	RUN			AVERAGE	GRADUATED VALUE, C	CALCULATED VALUE, C, BY EQUATION 1	ERROR
	13	14	15				
°C.							per cent
32.5					0.7946	0.7959	+0.16
35-45	0.793	0.793	0.795	0.794	0.7934	0.7933	-0.01
45-55	0.789	0.790	0.790	0.790	0.7902	0.7893	-0.11
55-65	0.785	0.787	0.785	0.786	0.7854	0.7846	-0.10
65-75	0.779	0.780	0.778	0.779	0.7799	0.7793	-0.08
75-85	0.775	0.775	0.774	0.775	0.7742	0.7734	-0.10
85-95	0.763	0.768	0.767	0.7675	0.7672	0.7668	-0.05
100					0.7563	0.7596	+0.44
102.8					0.7528	0.7575	+0.62

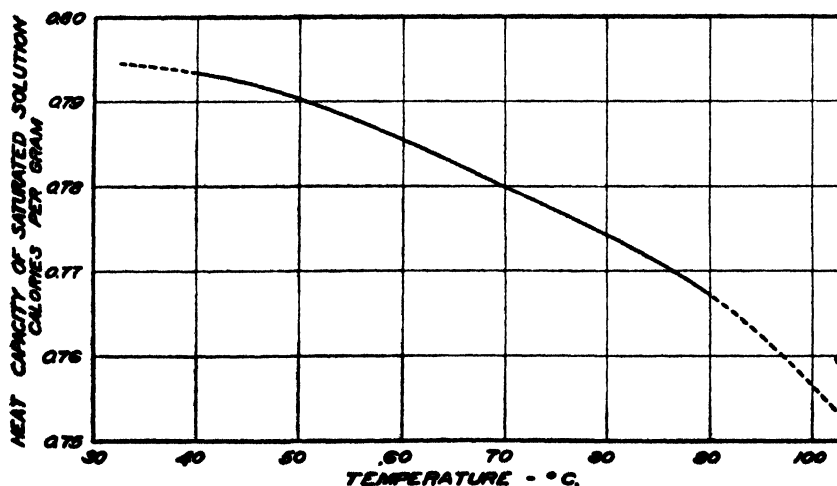


FIG. 1. Heat capacity of saturated sodium sulfate solution

calculations to account for the heat content of the anhydrous sodium sulfate precipitated from the solution as the temperature rises. The average amount of this salt (+1 g.) is determined by a graphical integration of the solubility curve. The heat content is then calculated for each temperature interval, using the heat capacity from the International Critical Tables (5).

The data are tabulated in table 1. From the average of values for the heat capacity a graduated value is determined by the method of Eggers (3). This method also gives a means of extrapolation which is used to give the heat capacity curve over the ranges 32.4° to 40°C. and 90° to 102.8°C. The graduated curve for heat capacity is shown in figure 1. This curve may be expressed by equation 1, where $t = ^\circ\text{C}$.

$$C = 0.803 - 1.14 \times 10^{-4}t - 3.2 \times 10^{-6}t^2 \quad (1)$$

The agreement between the values calculated by equation 1 and the graduated values is shown in table 1.

The mean heat capacity over the range 32.4° to 102.8°C. determined by graphical integration is 0.7796 cal. per gram. This value is very close to the 0.781 cal. per gram reported by Pagliani (8), who determined the heat capacity of 1 mole of sodium sulfate in 18 moles of water over the range 24° to 100°C. This system has an excess of the decahydrate up to 31°C., is unsaturated between 31° and 74°C., and has an excess of the anhydrous salt above 74°C.

MEAN HEAT CAPACITY, 20°C. TO 32.4°C.

Below 32.4°C. the saturated solution is in equilibrium with the decahydrate, for which the solubility curve rises steeply. Fifty milliliters of a solution saturated at 20°C. are pipetted into the calorimeter. Calculation shows 91.5 g. of sodium sulfate decahydrate will dissolve in this to give a solution saturated at 32.4°C. The decahydrate is added to the solution in four portions over equal parts of the temperature range. Room temperature is raised at the same rate as the temperature of the calorimeter to eliminate radiation and emergent stem correction. Corrections must be made for the excess decahydrate crystals present in the solution. Data are not available for the heat capacity of sodium sulfate decahydrate; Kopp's rule (4) may be used over this small range without great error.

The mean heat capacity may be calculated per gram of initial solution or per gram of average solution. The average weight of solution is found by graphical integration of the solubility curve over the range 20° to 32.4°C. The average weight must be corrected for the amount of unhydrated sodium sulfate in the decahydrate, as the hydrate readily effloresces.

From the data the mean heat capacities calculated are: 5.51 calories per gram of solution (average) and 7.92 calories per gram of solution (initial).

HEAT OF TRANSITION

Two values for the heat of transition are found in the literature. Cohen (2) found 16,509 cal. per gram-mole, and Leenhardt and Boutaric (7) found 18,400 cal. per gram-mole. The method used by both workers

started with the salt in solution and measured the heat of crystallization, which may be lower than the heat of transition as all of the heat of the crystal may not be given up immediately. The method used in this work was to measure directly the heat of transition.

Sodium sulfate decahydrate crystals are introduced into either nitrobenzene or toluene as the heat transfer liquid. The liquid is heated to 32.4°C., the decahydrate crystals added, and heat applied. As heat is applied, the temperature rises slowly until the transition is complete, then rises rapidly. By plotting temperature against time the intersection of the two lines gives the end of the transition. Correction is made for the heat necessary to bring the crystals from room temperature to the transition temperature. The heat capacity data for nitrobenzene as given in International Critical Tables (6) do not agree with those of Parks and Todd (9), whose data are used. The results are given in table 2.

TABLE 2
Heat of transition of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$

RUN	HEAT OF TRANSITION IN CAL. PER GRAM-MOLE	MEDIUM
9	18,800	Nitrobenzene
12	18,900	Nitrobenzene
13	18,900	Nitrobenzene
14	18,600	Toluene
15	18,600	Toluene
16	18,400	Toluene
17	18,700	Toluene
Average....	18,700	

The heat of transition may also be calculated from the vapor pressure data for the decahydrate crystals and the saturated solution by using the Clausius-Clapeyron equation. The value found by this calculation is 19,000 cal. per gram-mole.

Data, calculations, and corrections applied are too detailed to be given here, but may be found in the original report of the work (1).

SUMMARY

1. The heat capacity of saturated sodium sulfate solution from 32.4° to 102.8°C. may be represented by the equation

$$C = 0.803 - 1.14 \times 10^{-4}t - 3.2 \times 10^{-6}t^2$$

The mean heat capacity over this range is 0.780 cal. per gram.

2. The mean heat capacity of saturated sodium sulfate solution from 20° to 32.4°C. is: 5.51 cal. per gram of solution (average) and 7.92 cal. per gram of solution (initial).

3. The heat of transition of sodium sulfate decahydrate is 18,700 cal. per gram-mole.

REFERENCES

- (1) ANDERSON: Thesis, University of Washington, 1935.
- (2) COHEN: *Z. physik. Chem.* **14**, 53 (1894).
- (3) EGGERS: *Trans. Am. Inst. Chem. Engrs.* **27**, 334-74 (1931).
- (4) HOUGEN AND WATSON: *Industrial Chemical Calculations*, p. 211. John Wiley and Sons, New York (1931).
- (5) *International Critical Tables*, Vol. VII, p. 100. McGraw-Hill Book Co., New York (1930).
- (6) *International Critical Tables*, Vol. V, p. 110. McGraw-Hill Book Co., New York (1929).
- (7) LEENHARDT AND BOUTARIC: *Bull. soc. chim.* **13**, 651-7 (1913).
- (8) PAGLIANTI: *Atti Torino* **17**, 97 (1881-2); Landolt-Börnstein, *Physikalisch-Chemische Tabellen*, Vol. 2, p. 1262 (1923).
- (9) PARKS AND TODD: *J. Chem. Physics* **2**, 440-1 (1934).

THE THERMAL DISSOCIATION OF CALCIUM CARBONATE

J. C. SOUTHARD AND P. H. ROYSTER

Bureau of Chemistry and Soils, U. S. Department of Agriculture, Washington, D. C.

Received December 12, 1935

The thermal dissociation of calcium carbonate is a chemical reaction of considerable technical importance, not only in the case of the calcination of agricultural limestone as such, but in a number of fertilizer-production projects, such as the fixation of nitrogen as calcium cyanamide, and in the several proposed potash-volatilization processes. The experiments reported here were undertaken at this laboratory in connection with the development of a blast furnace method of producing potash from silicate rocks.

Several investigators (7, 10, 12) have shown that calcium carbonate dissociates into calcium oxide and carbon dioxide without the formation of an intermediate basic oxide and without solid solution of the resultant calcium oxide in the undissociated calcium carbonate. The atmospheric dissociation temperature has not hitherto been determined, however, with much accuracy. Among the more careful and recent measurements this temperature is given by Johnston (5) as 898°C., by Smyth and Adams (9) as 897°C., by Andrussow (1) as 882°C., and by Tamaru, Siomi, and Adati (10) as 882°C. While these observers differ by as much as 16°C. in their determination of the dissociation temperature, the heat of reaction at atmospheric pressure, as calculated from the pressure-temperature equation of these several investigators, varies about 1 per cent from a mean. The respective variations in temperature and slope of the $\log p$ curve suggest that the discrepancies were due largely to errors in temperature measurement.

In Andrussow's apparatus, the thermocouple was enclosed in the reaction chamber in an effort to measure the actual temperature of the dissociating carbonate. Andrussow, however, does not refer to the calibration of his couple or of his millivoltmeter. Tamaru, Siomi, and Adati used a calibrated thermocouple. Since they employed the Nernst quartz-fiber balance method, however, they were unable to place the couple inside the reaction chamber. It seems probable that this external couple was not at the temperature of the reacting carbonate, since the vessel and couple were inserted into the furnace to a depth of only three and one-half times the diameter of the enclosing quartz tube, and since neither baffles nor

other thermal protecting devices were used to minimize the thermal disturbance due to the circulation of room temperature air through the heated parts of the apparatus. Johnston discovered that his couple gave erroneous temperatures and attempted to correct for it.

DESCRIPTION OF APPARATUS

In the apparatus used in the present investigation, an improved type of reaction chamber, thermal environment, and temperature control was developed. Figure 1 shows a section of the central portion of the furnace. This furnace was 10 in. in outside diameter and 22 in. long, and was lined

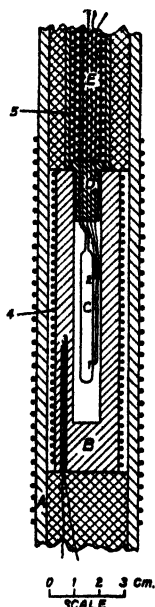


FIG. 1. The reaction tube

with $4\frac{1}{2}$ in. of insulating fire brick. A central alumundum tube (A), outside diameter 4 cm., was wound with a nichrome heating coil which served as the main heating resistance. A hollow nichrome block (B), 2.5 cm. in outside diameter and 12 cm. long, capped with a cover plate (D) carried a nichrome wire auxiliary heating resistance (4). A base metal thermocouple (3) was imbedded in a hole in block B and was in metallic contact with it. The E.M.F. in this couple was opposed by a constant external E.M.F.; a Leeds and Northrup high sensitivity galvanometer was used as a null instrument; light reflected from the galvanometer mirror actuated a photocell which controlled, by a relay, the current through the auxiliary heater (11). This device held the block at 900°C . for more than thirty hours with a maximum variation of 0.04°C . from its mean temperature.

It was found necessary to provide a third heating coil, the stem heater labelled 5 in figure 1, in order to prevent a cold spot appearing at block D due to upward radiation. A thin-walled platinum reaction chamber (C), 50 mm. long and 5.0 mm. in outside diameter, was located within block D and was connected with the external pressure-measuring system by a 1-mm. bore platinum tube E. All connections in this part of the apparatus were gold-soldered.

The principal thermocouple (platinum 10 per cent rhodium platinum) was gold-soldered to the reaction chamber at a lower point (indicated by the numeral 1 in figure 1). This couple had been calibrated at the Bureau of Standards. On the basis of this calibration the melting point of gold was found in our apparatus prior to the installation of the reaction tube to be $1062.9^{\circ}\text{C}.$ ($1063^{\circ}\text{C}.$ melting point of gold, 1927 International Temperature Scale). A second 10 per cent rhodium platinum wire was gold-soldered to platinum chamber C at an upper point (point 2), and in connection with the rhodium platinum wire at point 1 served as a difference couple. Hand regulation of the current in the stem heater 5 prevented a temperature

TABLE I
Dissociation pressure of calcium carbonate

TEMPERATURE IN $^{\circ}\text{C}.$	PRESSURE IN CM. OF MERCURY (OBSERVED)	PRESSURE IN CM. OF MERCURY (CALCULATED)	DIFFERENCE OBSERVED MINUS CALCULATED
900.3	82.60	82.68	0.08
877.8	59.87	59.83	+0.01
854.6	42.23	42.23	0.00
774.8	10.93	11.21	0.28

difference between points 1 and 2 of more than $0.05^{\circ}\text{C}.$ Pressure within chamber C was read on a mercury manometer having an internal diameter of 10 mm. This manometer tube was mounted in front of a mirrored glass scale which had been calibrated at the Bureau of Standards. Pressure readings were reduced to $0^{\circ}\text{C}.$, and a gravity correction of 0.44 mm. per atmosphere applied. These readings were probably accurate to 0.1 mm. of mercury. Before admitting mercury to the manometer, the reaction chamber containing the carbonate sample was heated to $300^{\circ}\text{C}.$, pumped down by a mercury diffusion pump, and outgassed overnight at a pressure of 10^{-5} mm. of mercury as read on a McLeod gauge.

RESULTS

The carbonate sample was taken from an optically clear crystal of calcite from Minnesota. Analysis showed the crystal to contain 0.011 per cent of magnesium oxide. A sample weighing 0.773 g., crushed to about 100 mesh, was placed in chamber C, filling it approximately half full. The sample was subjected to thermal dissociation, the carbon dioxide evolved

was measured in a buret, and the composition of the solid phase used in these measurements was found to be approximately 80 per cent calcium oxide and 20 per cent calcium carbonate, as calculated from the measured carbon dioxide removed. In the case of each equilibrium pressure shown in the table, the temperature was maintained constant from one to two days. In each case equilibrium was approached from both sides.

The pressure-temperature relation recorded in table 1 may be represented by the equation

$$\log_{10} p_{\text{cm.}} = \frac{-9140}{T} + 0.382 \log_{10} T - 0.668 \times 10^{-3} T + 9.3171 \quad (1)$$

The linear relation

$$\Delta C_p = 0.76 - 0.0061 T \quad (2)$$

was assumed to represent ΔC_p for the dissociation reaction (2, 3, 4, 6, 8) in the temperature range (900–1200° K). The coefficients of the third and fourth terms in equation 1 were taken from equation 2. The second and fifth terms of equation 1 were adopted to give agreement with the observations as indicated in the table.

Calculated from equation 1, the atmospheric dissociation temperature is 894.4°C. and should be correct to better than 0.3°C. This temperature is 12°C. higher than the 882°C. obtained independently by Andrussov and by Tamaru, Siomi, and Adati. It is 2.6°C. lower than the 897°C. obtained by Smyth and Adams, which may be within their probable error. From equation 1

$$\Delta H_{1167.6}^0 = 38,550 \text{ cal.}$$

SUMMARY

1. A furnace was constructed containing a reaction chamber which was maintained isothermal within 0.04° at 900°C. for more than thirty hours.

2. The temperature at which the dissociation pressure of calcium carbonate equals one atmosphere was found to be 894.4°C.

REFERENCES

- (1) ANDRUSSOW: *Z. physik. Chem.* **116**, 81 (1925).
- (2) BÄCKSTRÖM: *J. Am. Chem. Soc.* **47**, 2432 (1925).
- (3) ESSER, AVERDIECH, AND GRASS: *Arch. Eisenhüttenw.* **6**, 289 (1933).
- (4) GRONOW AND SCHWIETE: *Z. anorg. Chem.* **216**, 188 (1933).
- (5) JOHNSTON: *J. Am. Chem. Soc.* **32**, 938 (1910).
- (6) KASSEL: *J. Am. Chem. Soc.* **56**, 1838 (1934).
- (7) RIESENFELD: *J. chim. phys.* **7**, 561 (1909).
- (8) ROTH AND BERTRAM: *Z. Elektrochem.* **35**, 297 (1929).
- (9) SMYTH AND ADAMS: *J. Am. Chem. Soc.* **45**, 1167 (1923).
- (10) TAMARU, SIOMI, AND ADATI: *Z. physik. Chem.* **157**, 447 (1931).
- (11) ZABEL AND HANCOX: *Rev. Sci. Instruments* **5**, 28 (1934).
- (12) ZAVRIEV: *Compt. rend.* **145**, 428 (1907).

THE CREEPING OF SATURATED SALT SOLUTIONS

T. H. HAZLEHURST, JR., H. C. MARTIN, AND L. BREWER

Department of Chemistry, Lehigh University, Bethlehem, Pennsylvania

Received October 25, 1935

INTRODUCTION

Two studies of creeping have been recorded. E. R. Washburn (4) tried various solutions and solid surfaces and noted the general nature of the phenomenon. He observed that creeping is found not only in aqueous solutions of electrolytes, but also in non-aqueous solutions (e.g. sulfur in carbon bisulfide), and occurs not only on glass, but also on porcelain and metals. J. G. F. Druce (1), in common with Washburn, found quantitative results practically impossible because of the large number of variables, but submitted a list of substances "in descending order of creeping:" ammonium chloride, zinc sulfate, barium chloride, potassium nitrate, manganous sulfate, sodium chloride. Druce does not describe his experiments. Washburn seems to have worked with solutions evaporating in dishes. The latter offers as an explanation of the phenomenon the formation of capillaries by the deposited crystals, up which the solution may rise with the subsequent deposition of more crystals and the formation of new capillaries. It is difficult to picture how the capillaries are formed originally, for the protrusion of the crystals beyond the limits of the solution seems much like raising oneself by one's bootstraps. The present authors find that creeping does not *start* by the formation of capillaries, although these undoubtedly contribute largely to the maintenance of vertical creeping. The prime factor in the production of creeping is the ability of the *solid solute to wet preferentially the solid surface over which the creeping takes place.*

EXPERIMENTS

To obtain a quantitative estimate of the height to which a creeping solution will climb, glass rods, thoroughly washed and repeatedly rinsed with distilled water, were suspended with the lower end of each rod under the surface of a saturated solution of either ammonium chloride, potassium chloride, sodium chloride, or potassium iodide. The apparatus was placed under a bell jar to insure as far as possible uniform conditions of evaporation. Concentrated sulfuric acid served as a drying agent. Table 1 shows the numerical results obtained.

In agreement with the results of Druce, ammonium chloride is the "best"

creeper. However, the numbers listed are rough averages. Three rods were suspended in each solution and the average height to which the solute climbed was recorded. In spite of every care to insure nearly uniform conditions, results could not be checked by subsequent experiment, except in the case of potassium chloride. In fact, the three rods suspended simultaneously in the same solution would be covered to heights differing by an inch or more. This shows that a control of the usual macroscopic variables is insufficient to secure concordant results. Doubtless such practically uncontrollable factors as local concentration and temperature conditions in the immediate neighborhood of a deposited crystal have a great influence upon the rate and character of succeeding deposits there.

It was evident that creeping was of two sorts. Along the rod itself and closely adherent to it was a layer of very fine crystals. Once creeping had commenced, the upper edge of this crystal mass was added to fairly regularly. At intervals this process was halted temporarily and more

TABLE 1
Creeping on glass rods

SOLUTE	HEIGHT IN INCHES AFTER		
	18 hours	24 hours	90 hours
KI ..	1 3	1 9	2 5
NaCl	0 0	0 6	1 5
KCl	3 0	3 0	3 0
NH ₄ Cl	2 5	3 0	3 6
NH ₄ Cl*	2 0	2 5	3 3
KCl	3 0	3 0	3 0

* This solution contained 1 per cent gelatin.

crystals would grow outside the first layer. The first layer was regular and even; the second and succeeding layers grew in localized regions and irregularly. Dome-shaped, pyramidal, or cauliflower-like growths appeared, and not infrequently "hair crystals" (2, 3). Ammonium chloride was particularly prolific in this respect. The distinction between the two sorts of creeping was even more evident when studied microscopically.

Very frequently deposition of crystals took place in the bulk of the solution continuously for some time (e.g., eighteen hours in the case of sodium chloride) before creeping commenced. Invariably, as far as the eye could detect, crystallization began on the surface of the rod well *below* the surface of the solution before creeping was visible. According to Washburn's explanation of creeping, the rod, which was certainly clean and wet with the solution, should have allowed creeping immediately, and there should have been no necessity for the presence of crystals well beneath the surface to initiate the process.

When drops of the solutions were evaporated upon glass slides, the deposited crystals were found over an area far larger than that of the original drop. That they found their way out over the slide by a mechanism identical with that by which they crept up rods or the sides of beakers

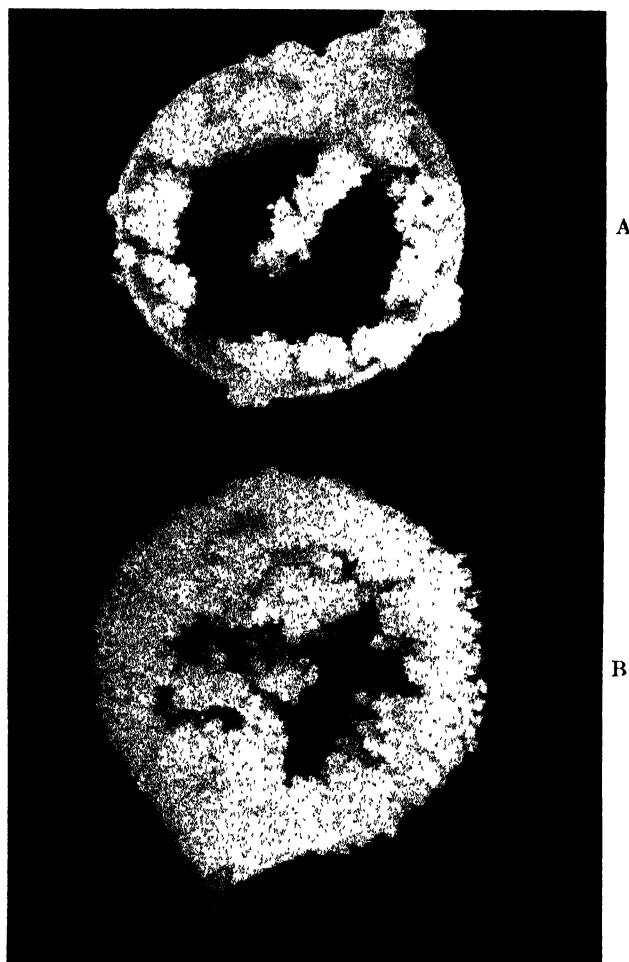


FIG. 1. Beakers containing ammonium chloride solution which was allowed to evaporate freely: (a) evaporation in progress; (b) after reaching dryness

was evident. This arrangement made possible microscopic observation of the process using magnification up to 500 times. Invariably creeping was preceded by crystallization in the interior, and began at those points where the crystals approached and thrust against the edge of the drop.

Note in figure 2a how the uppermost crystal of potassium chloride appears to be pushing or stretching the edge of the drop.

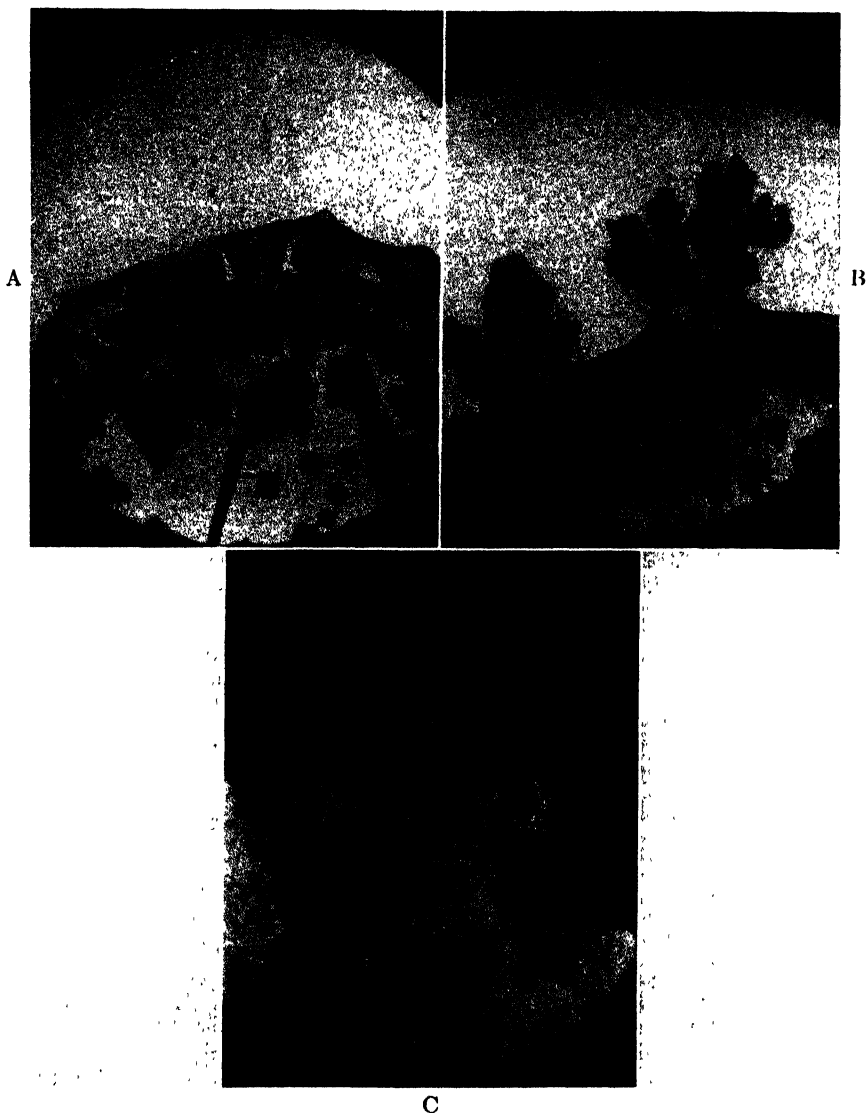


FIG. 2. Photomicrographs, taken at intervals of a few seconds, of the beginning and progress of creeping in a drop of potassium chloride solution. 2a and 2b were taken with bright field illumination; 2c with dark field.

In many drops, especially of solutions of ammonium chloride and the alkali halides, another curious thing took place. The advance of creeping

was regular and fairly rapid until suddenly there occurred a "flooding." The advancing mass¹ of crystals was very suddenly broken up and inundated by a relatively large quantity of solution. In about half the cases of flooding the very outermost ring of material is unaffected, remaining fixed in position during the whole process until creeping begins again. In other cases the outer edge is also loosened and is *swept back towards the center of the drop*. After flooding occurs, creeping ceases until the loosened mass becomes compact again through settling and the deposition of further

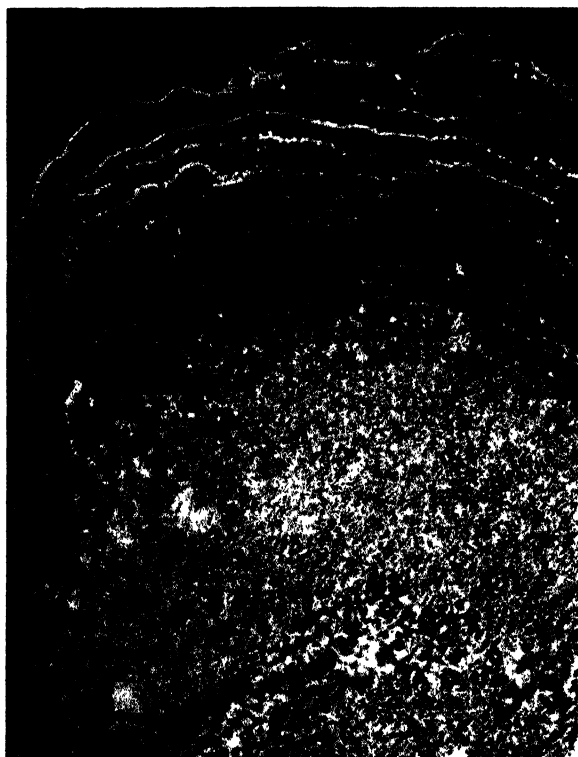


FIG. 3. Illustrating the traces of the periodic flooding phenomenon

crystalline material. Flooding is invariably localized. Regular creeping occurs at other points of the periphery even while flooding is proceeding at certain points. The crystal mass loosened by flooding and subsequently reconsolidated is noticeably thicker than the unflooded portions. Each successive flooding produces a new thickening, and it is possible to look

¹ Of course the crystals themselves do not move while creeping is going on. The outer edge of the deposited material advances because new crystals grow beyond the limits of those already there.

at a dried drop and tell how many floodings occurred during the creeping (cf. figure 3). A similar appearance was observed in the material which had climbed the glass rods in the previous experiments.

Negative results were obtained when a definite rhythm was sought in the floodings. Although a certain tendency towards a definite time interval between floodings could be traced in a given region of a given drop, the interval bore no simple relation to those observed even in other portions of the same drop. Some drops went to complete dryness without observable flooding at all.

MECHANISM OF CREEPING

The hypothesis which seems to the authors most fruitful in explaining the phenomena connected with creeping is as follows. A drop of solution, becoming supersaturated by evaporation, will deposit crystals wherever there are nuclei. Since these are not necessarily at the edge of the drop, crystals often appear first in the interior. No crystals will form outside the drop, for the reason that no solution and so no solute exists beyond the drop.² This applies with equal force to the possibility of crystallization beyond the visible limits of the solution in the common case of creeping up the wall of a dish. The notion that crystallization can occur there and so form capillaries up which the solution may climb appears highly improbable.

The small crystals first formed in the interior of the drop may be and frequently are drawn by the action of surface forces to the three-phase line where solution, glass, and air meet. It often happens that crystals are formed near this line, because the convex surface of the drop nearby promotes evaporation and so local supersaturation, which favors crystallization. The crystals now have the opportunity, if the interfacial tensions are of the proper magnitude, of wetting the glass preferentially, i.e., of coming into intimate or optical contact with it, no solution or solvent intervening. The solution touches and wets the glass all around but not under the crystal. The crystal will grow most rapidly in the direction away from the drop, because crystallization is most rapid in the thin film of

² It is true that aqueous solutions "wet" glass, but the angle of contact is almost never zero in practice, and is certainly not so when a drop will maintain its shape and not spread to form a film of uniform thickness. The possibility of a monomolecular film, or even a very thin polymolecular film, over the slide beyond the limits of the drop is not entirely precluded, but the film, if it exists, contains a wholly negligible amount of solute for two reasons: (1) in aqueous electrolytic solutions the solute is negatively adsorbed to the surface, and the film would be, in a manner of speaking, all surface; (2) spreading to such a thin film probably occurs by evaporation and subsequent recondensation at favorable points, a procedure which is impossible for the solute (cf. N. K. Adam, *The Physics and Chemistry of Surfaces*, Oxford University Press, 1930).

solution covering the outer edge of the crystal. The growth of the crystal in this direction carries the solution along with it. The crystal grows outwards, covered by a layer of solution which extends beyond the advancing edge and there acts as a mother liquor for the growth of the crystal already formed and for the formation of new ones if nuclei appear. The layer is constantly replenished from the body of the drop.

Such a growth on a horizontal slide where what small effect gravity has would assist the spreading, might conceivably continue steadily until all the solvent had evaporated, and this does happen in the absence of flooding. Not infrequently the area originally occupied by the drop is almost bare of deposited crystals at the end, practically the entire mass of solution having followed the creeping crystals.

It may be noted in the various illustrations that the creeping mass is very compact and that there are certainly no obvious capillaries. It is highly probable that there are no capillary spaces *beneath* the outer crystals. The solution is advancing *over* them, not through or under them.

If some fault in the mass permits the liquid to penetrate it and reach the slide, thus getting *under* the crystals, there is a sudden and violent alteration of surface energy relations. The mass is broken up as far as it can be loosened by the shock. The advanced edge of the solution experiences a force tending to make it assume more or less the position it originally occupied. The tiny individual crystals become separated and tend to be pulled back to the main body of the drop. This is evidence that if the crystals were not in intimate contact with the slide, creeping would not take place.

The fact that flooding is sometimes absent shows that it is not an essential part of creeping but is caused by fortuitous circumstances, say the existence of a very minute speck of impurity on the slide which prevents the crystal from making optical contact.

It often happens that little knobs and other growths appear in the crept material on the slide just as they do in material which creeps on rods. They are especially frequent in the thicker regions where flooding has occurred. They represent the "efflorescent" creeping, i.e., creeping upon previously deposited crystals. Both solution and solute will be able to wet such a surface readily. In spite of this it is usually true that the major portion of the material is to be found in the smooth "mural" creeping (creeping directly along the wall), and only a small part in the knobs. This is due in large part to the relative *smoothness* of the surfaces. Freshly grown crystal surfaces, being nearly plane, can come into intimate contact with smooth surfaces far more readily than with rough. The glass plate or rod is smooth, while the mass of small crystals, oriented more or less at random, is rough. In following the rough surfaces such growths as do occur may proceed in any direction, even vertically. In the process of

flooding and subsequent reconsolidation it is readily conceivable that some droplets of solution may become trapped and have no outlet for depositing crystals except upwards.

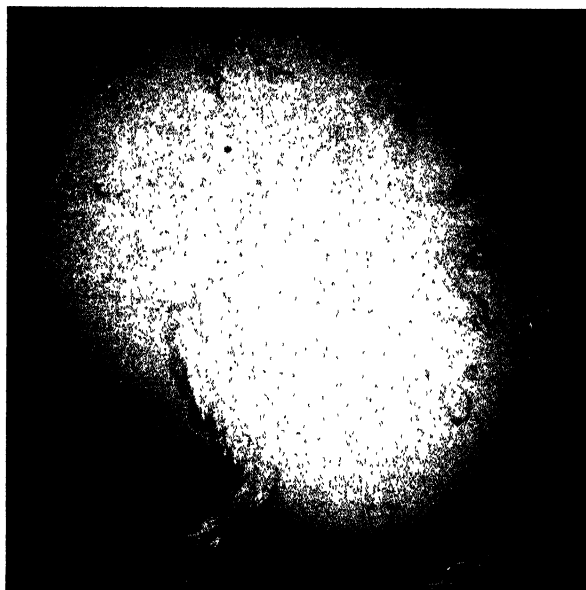
Drops were allowed to dry simultaneously upon (i) a polished slide, (ii) a slide etched by hydrofluoric acid, and (iii) a slide ground upon a fine stone. In every case creeping was definitely less pronounced upon the rough than upon the smooth surface. This may seem surprising, because liquids will spread farther upon rough than upon smooth surfaces because of the capillary attraction of the pits and grooves. That creeping occurs less readily upon surfaces which are more easily wet by the solution itself is good evidence that it is the ability of the *solid solute* to advance by wetting the surface that is the primary factor.³ In support of these experiments it was found that the addition of wetting agents such as gelatin and gardinol caused the liquid drop to be flatter but had no effect upon the extent of creeping, as judged by the relation between the area of the drop and the area covered by creeping.⁴

The effect of gravity was ascertained to be negligible by allowing drops to dry upon slanting slides or even hanging from the bottom. No significant effect was observed. Surface effects take precedence entirely. Washburn (4) remarks that after crystallization has proceeded up to the rim of a dish and has started down the outside the advance is accelerated, because the solution "siphons" out and gravity helps instead of hindering. This has not been the experience of the authors in the relatively few cases in which they studied creeping out of beakers. If a glass rod be allowed to rest against the side of the beaker, creeping seems to proceed just about as readily *up* the rod above the rim as over the rim and *down* the beaker (cf. figure 1).

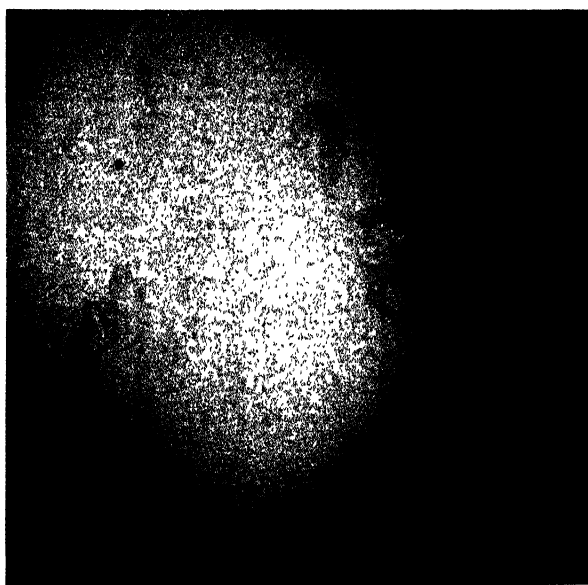
The following observation affords direct evidence that the solid solute wets the slide. If a drop of solution is allowed to dry, and the slide is examined from *beneath*, it will be noticed that there is a distinct difference between the outer edge of the crept crystals and the remainder of the deposited solute. Let the slide be held in such a position that it reflects the light from a patch of sky or a frosted bulb. If there are no crystals on the slide, light will be reflected uniformly from both surfaces of the slide.

³ Washburn (4) notes that sulfur in carbon bisulfide creeps readily over metallic copper "in spite of" the fact that a deposit of sulfide of copper immediately forms. This is merely an extreme case in which the solute "wets" the supporting surface chemically.

⁴ Quantitative results are hard to obtain. Ratios such as that mentioned were measured for fifty drops nearly identical in magnitude and conditions of evaporation. They varied from 2.78 to 11.61, with a mean of 6.12 and a mean deviation of 1.72. All conclusions recorded in this paper have been drawn from a large number of experiments in order to obtain a reliable average. Quantitative conclusions drawn from a single experiment are entirely untrustworthy.



A



B

FIG. 4. Showing that the outer rim of crystals which have crept on a slide is in very intimate contact with the slide

If the air beyond the farther surface is displaced by a crystal or any other medium of large refractive index, the amount of light reflected is cut down considerably. Hence those portions of the farther surface with which the crystals are in *optical contact* will appear relatively dark. It is always the *outer rim* of crept material which gives this effect, as shown in figure 4a.⁵ Figure 4b shows the same slide in the same position, but after the crystals had been rubbed off as well as possible with the ball of the thumb. It is typical that the outer rim of crystals should resist removal by rubbing, another indication of the extremely intimate contact of these crystals with the slide. They must be *scraped* off with the finger nail. The closely adherent crystals are evidently those which appeared dark in the first picture. It is clear that the outer rim of crystals has a close hold upon the slide and pulls the liquid with it as it grows.

FACTORS INFLUENCING CREEPING

Among the factors governing the extent of creeping, crystal habit is one of the most important. Ammonium chloride is typically dendritic and creeps rapidly. On the contrary, potassium nitrate forms rod-like crystals and so grows preferentially in one direction. Hence ammonium chloride usually creeps to form a roughly circular mass conforming to the shape of the drop, while potassium nitrate forms a few directed masses.⁶ Further, the formation of a relatively simple structure of few units similarly directed offers less opportunity for flaws leading to flooding. Ammonium chloride floods habitually, potassium nitrate only exceptionally. The alkali halides, which are cubic like ammonium chloride but not usually dendritic, do not creep as readily as ammonium chloride.

The nature and structure of the supporting surface is obviously important. Smooth surfaces are better for creeping than are rough. It is also evidently necessary that the solution wet the surface or it would not advance in front of the crystals. It was found that ammonium chloride solutions crept decreasingly well on the following surfaces: glass, stearic acid, vaseline, paraffin, sulfur. This is about the order in which these surfaces are wetted by water.

⁵ This photograph was obtained as follows. Light from a frosted Mazda bulb was reflected by means of an inclined glass plate down upon a slide bearing on its under surface the crystals formed during the evaporation of a drop of potassium nitrate solution. The light reflected from the slide passed back through the glass plate into the camera vertically above the slide. Superposed upon the image of the bulb can be seen the dark regions where the crystals are in optical contact. The other crystals can be seen faintly by scattered illumination.

⁶ It may be of interest to note that observation of the deposited potassium nitrate between crossed Nicols shows that the major portion of the material in one of the directed masses has the optical axis similarly directed, although the thickness varies from point to point and observation with ordinary light shows a number of separate crystals.

Even if the supporting surface can be wetted by both solute and solution, creeping may not occur. If the free surface energy of the crystal-solid interface is greater than the combined free surface energies of the solution-solid interface and the solution-crystal interface, the crystalline solute cannot wet the solid surface preferentially and creeping cannot commence.

The above applies to creeping directly along the wall,—“mural” creeping. It is possible, however, for creeping solutes to cross a barrier of, say, sulfur, as follows. By “efflorescent” creeping the solute builds up a wall of material at the edge of the barrier. Such walls have been observed to grow to heights of over 2 mm. on slides. By a continuation of efflorescent creeping parallel to, but not in actual contact with, the supporting surface,

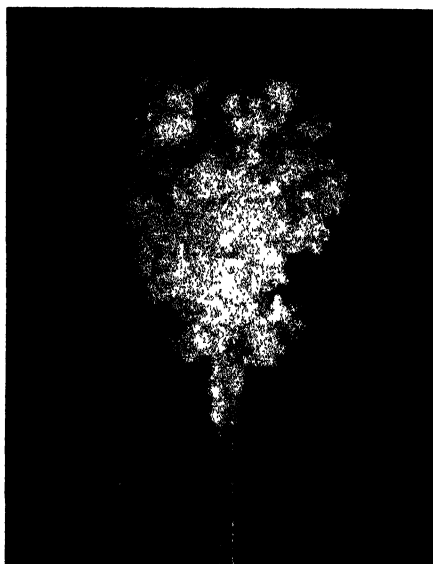


FIG. 5a Knob of ammonium chloride crystals formed on the end of a glass capillary of about 1 mm. outside diameter

the solute advances almost indefinitely. If the barrier is narrow and other circumstances are right, mural creeping may recommence on the other side of the barrier. Narrow barriers actually do not prevent creeping.

When the solute is creeping upwards along a beaker wall the formation and maintenance of capillaries must be important. It is probable that strictly mural creeping must be supplemented by floodings which loosen the mass a little, permitting the formation of capillaries. A somewhat violent flooding might seriously damage the layer of crystals at a particular point and induce efflorescent creeping there. In figure 1 are two beakers of ammonium chloride solution, one just approaching dryness and the other dry. Note the localized growths, particularly on the stirring rod

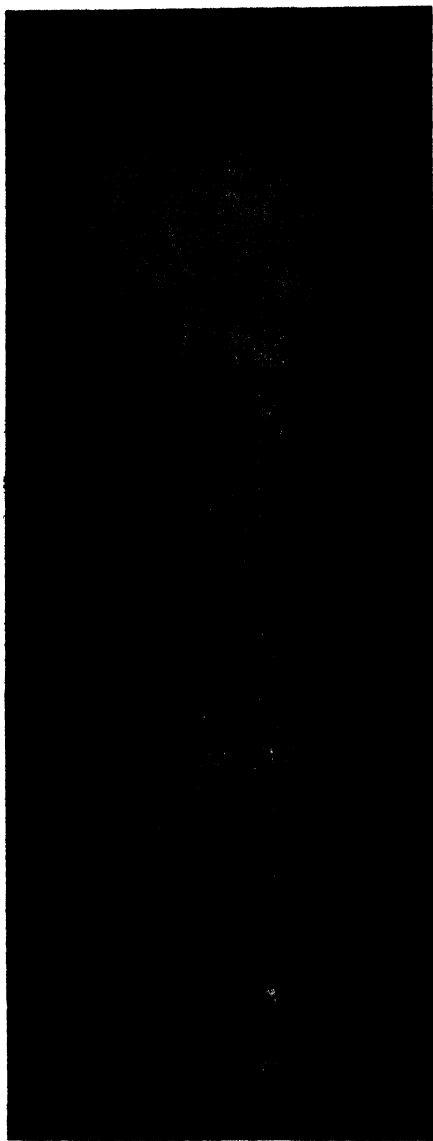


FIG. 5b. Potassium nitrate crystals grown on the end of a glass capillary of about 1 mm. outside diameter. Note the sheath of crystalline material along the outside of the tube and the numerous and complicated growths of "hair crystals."

in the first beaker, and the consolidated mass of growths in the other. The capillaries serve to keep the advancing edge supplied with solution and they fail to do this if they become either too wide or clogged, as Washburn has pointed out.

EFFLORESCENT STRUCTURES

The crystalline structures formed by efflorescent creeping are interesting and worthy of study. If a very fine glass capillary is allowed to stand in a saturated solution of ammonium chloride or potassium nitrate to such a depth that the solution will rise to the top of it, crystals are deposited there. In some cases knobs of material are formed (figure 5) and practically no creeping *down* the outside of the tube occurs. Once a spherical mass of potassium nitrate crystals over $\frac{3}{4}$ " in diameter was obtained. In other

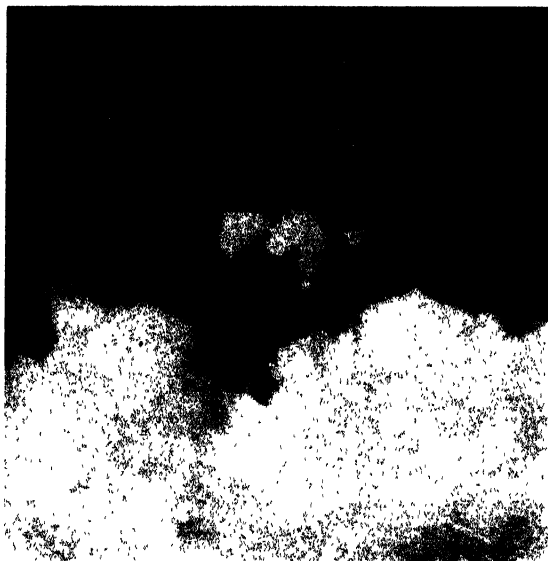


FIG. 6. "Hair crystals" of potassium chloride. Note the resemblance to figure 5a. The hair crystal is hollow and has grown a knob on top

cases creeping down the tube also takes place, and in both cases hair crystals are frequently formed (figures 5 and 6). The formation of hair crystals without the use of collodion or silica gel is being studied.

SUMMARY

The previous work of Washburn and of Druce has been extended, and a few roughly quantitative results obtained. The hypothesis advanced by them as to the mechanism of creeping has been extended to explain the formation of the capillaries they assume. Creeping is supposed to occur when the *solute* is capable of displacing the solution from, and spreading over, the supporting surface. Creeping is commonly accompanied by "flooding," a process which loosens the compact mass and permits capillaries to form. The solution rises *through* the capillaries and *over* the

outermost edge of deposited material, which has been shown to be in optical contact with the surface.

The effect of the nature of the supporting surface, of the crystal habit of the solute, and of the various free surface energies involved has been discussed.

Certain curious crystal formations have been noted.

REFERENCES

- (1) DRUCE, J. G. F.: *Pharm. J.* **119**, 333 (1927).
- (2) HINEGARDNER: *J. Am. Chem. Soc.* **55**, 1461 (1933).
- (3) TAUBER AND KLEINER: *J. Am. Chem. Soc.* **54**, 2392 (1932).
- (4) WASHBURN, E. R.: *J. Phys. Chem.* **31**, 1246 (1927).

ISOELECTRIC POINT OF GLYCININ¹

R. J. HARTMAN AND L. T. CHENG²

Department of Chemistry, Indiana University, Bloomington, Indiana

Received November 15, 1935

INTRODUCTION

There are two different points of view with regard to the relationship between the minimum physical properties and the isoelectric point of a protein. Loeb (4), who studied gelatin, concluded that at the isoelectric point the physical properties of a protein are all at a minimum. Michaelis (5) developed a theory according to which the solubility of an amphoteric substance is directly proportional to the ionization, so that at the isoelectric point the solubility must be at a minimum. An entirely different opinion concerning the relationship between the isoelectric point and the minimum physical properties of gelatin is held by Johlin (2). He reported that there is no definite relationship between the minimum physical properties and the isoelectric point of gelatin, as pointed out by Loeb and Michaelis. Very recently, however, Pedersen (7) found that the pH at the minimum solubility of certain blood proteins (helix, hemocyanin) coincides with their isoelectric points.

No record, hitherto, can be found in the literature concerning the isoelectric point of glycinin. It is the purpose of this investigation to determine the isoelectric point of glycinin, i.e., the point at which the negative and positive charges carried by the glycinin particles are equal; and, furthermore, to study the relationship that exists between the isoelectric point and the minimum of certain physical properties such as viscosity, solubility, and conductivity.

EXPERIMENTAL

Materials

The glycinin used in this study was prepared by the modified Osborne and Clapp method (6). It was twice purified by dissolving in 10 per cent

¹ This is one of two papers constructed from a dissertation presented by Libin Tsi Cheng to the Faculty of the Graduate School of Indiana University in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry, June, 1934.

² Chief Research Biochemist, Department of Physiological Chemistry, the Science Society of China, Nanking, China.

sodium chloride solution, filtering, dialyzing, and finally treating with methyl alcohol and ether.

Method of procedure

The isoelectric point of glycinin was found by means of electrophoresis. The pH values at which the glycinin solution showed minimum physical properties were also measured.

(a) *pH measurements.* The pH values reported in this paper were all measured by means of the hydrogen electrode at 25°C. ($\pm 0.1^\circ$). In some cases these values were checked with measurements made with the quinhydrone electrode at the same temperature.

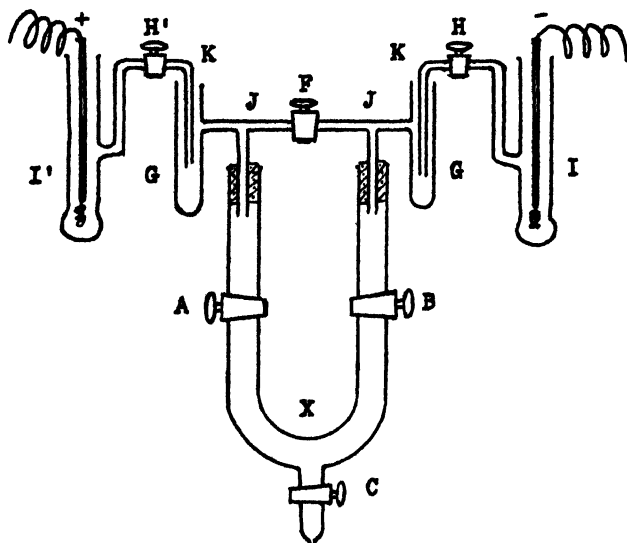


FIG. 1. The apparatus

(b) *Electrophoresis.* The apparatus and method of Sherman, Thomas, and Caldwell (8), slightly modified by the authors, was used in this study. A sketch of the apparatus is shown in figure 1. The procedure employed is described as follows: A 0.5-g. sample of glycinin was dissolved in 50 ml. of 1 per cent sodium chloride solution in a 125-ml. Erlenmeyer flask. The mixture was shaken for 20 minutes and then filtered. More 1 per cent sodium chloride solution was added to bring the volume of the filtrate to 50 ml. Fifteen milliliters of the protein solution thus prepared was taken for each determination and was drained into a large Pyrex test tube to which was added 15 ml. of buffer mixture of definite pH. Potassium phthalate-sodium hydroxide buffer mixtures of various pH were prepared according to Clark (1). This resulting solution was thoroughly mixed

and its pH measured. Twenty-five milliliters of the protein-buffer mixture was then pipetted into the U-tube (figure 1); this quantity just filled the bend, x, and the stopcocks, A and B. After all the bubbles were excluded, the stopcocks A and B were closed. The two arms above the stopcocks were washed with distilled water and filled with buffer solution of the same pH as was used in preparing the protein-buffer mixture. The leveling bridges (J) and the connecting flasks (G) were then inserted. Buffer solution of the same pH was used to fill the entire bridge. This was accomplished by opening the stopcock, F, adding the buffer solution to one end, and letting it flow through the bridge to the other end. The electrode vessels (I and I') and their bridges (K) were also filled with the same buffer solution and inserted in the connecting flasks (G). Solid copper sulfate and a copper electrode were placed in vessel I, and solid potassium biphthalate and a platinum electrode were placed in vessel I'. When the whole apparatus was assembled as shown in figure 1, the stopcocks H, H', and F were opened in order to adjust the level in the whole system. A 110-volt direct current was turned on while the stopcocks, H, H', and F were still open and the stopcocks A and B closed. The stopcocks H and H' were then loosely closed, so that a film of the buffer solution surrounded them, thus conducting the current. The stopcock F was then closed as tightly as possible. Stopcocks A and B were then opened simultaneously. The electrophoresis was continued for twenty-four hours in each determination and at 20°C. ($\pm 1^\circ$). At the end of twenty-four hours the stopcocks A and B were both closed simultaneously, the current broken, and the other parts disconnected. The solution present in each arm of the U-tube was then poured carefully into two large test tubes. The arms were rinsed thoroughly with distilled water. The solution in the bend of the U-tube was emptied through stopcock C with stopcocks A and B open. The pH of the latter solution was determined again. Five milliliters of the solution from each arm of the U-tube was used to determine the nitrogen content by the Koch-McMeekin-Kjeldahl method (3).

(c) *Solubility measurements.* In order to determine the solubility of glycinin, 10 ml. of a 1 per cent solution of glycinin prepared by dissolving 1 g. of glycinin in 100 ml. of 1 per cent sodium chloride solution was mixed with 10 ml. of a buffer mixture of desired pH. The mixture was shaken for five minutes and then centrifuged for ten minutes. The clear liquid part was decanted into a dry test tube. Five milliliters of this clear liquid was taken for total nitrogen determination by the Koch-McMeekin-Kjeldahl method (3). A Duboscq colorimeter was used in determining the nitrogen content of the solution. The solubility is expressed in terms of the per cent nitrogen in solution (table 2).

(d) *Viscosity determinations.* Ten milliliters of the 1 per cent protein solution was mixed with 10 ml. of buffer mixture. After shaking for ten

TABLE 1
Electrophoresis of glycine

pH OF PROTEIN SOLUTION BEFORE ELECTROPHORESIS	N IN MG. PER 500 ML. IN CATHODIC SOLUTION	N IN MG. PER 500 ML. IN ANODIC SOLUTION
4.25	15.0	2.3
4.43	6.4	6.0
4.63	6.2	5.8
4.83	5.7	5.5
4.94	3.7	3.4
5.02*	2.2	2.3
5.11	3.6	3.8
5.23	5.5	5.6
5.42	5.2	6.3
5.63	6.0	6.6
5.83	6.4	8.8
6.05	6.5	9.0
6.28	2.0	10.5

* Isoelectric point = pH 5.02.

TABLE 2
Solubility of glycine

pH	DUBOSCQ COLORIMETER READING OF UNKNOWN*	N IN MG. PER 50 ML.
3.25	12.0	5.00
3.45	13.4	4.48
3.65	14.4	4.17
3.85	15.4	3.90
4.05	16.4	3.66
4.23	17.4	3.45
4.43	18.4	3.21
4.63	20.5	2.93
4.83	21.4	2.81
5.02	23.1	2.60
5.42	22.4	2.68
5.63	15.0	4.00

* The standard reading in each instance was 20.

TABLE 3
Viscosity of glycine

pH	TIME OF FLOW* IN SECONDS	pH	TIME OF FLOW IN SECONDS
3.6	85.0	4.6	83.0
3.9	84.5	4.8	80.0
4.0	84.0	5.0	79.8
4.2	83.8	5.2	82.1
4.4	81.0	5.4	88.0

* All determinations were checked several times, using two different Ostwald viscosity pipets at 25°C. ($\pm 0.1^\circ$).

minutes, the time of flow of this solution was determined by means of an Ostwald viscosity pipet at 25°C. The pH was also determined in each case at the same temperature.

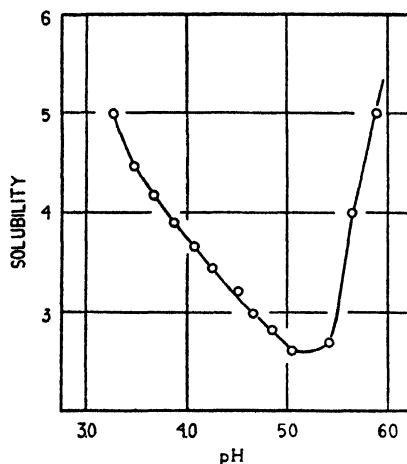


FIG. 2. Solubility of glycinin at different pH values

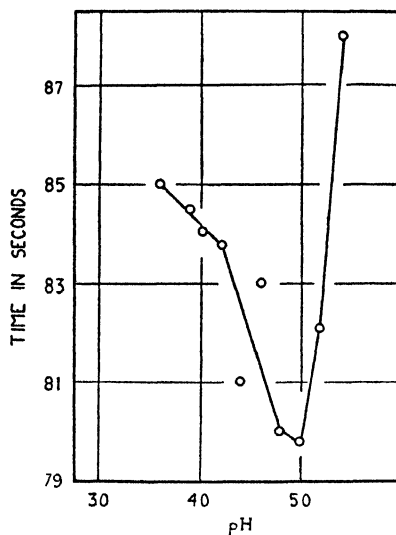


FIG. 3. Viscosity of glycinin at different pH values

(e) *Conductivity measurements.* In making the conductivity measurements the resistance of the mixtures of 10 ml. of 1 per cent glycinin solution and 10 ml. of each buffer mixture was measured in the usual way. The resistance of each buffer solution employed was also determined in order to obtain by difference the conductivity due to protein.

TABLE 4
Conductivity of glycinin

pH	<i>R</i> BUFFER ALONE	<i>R'</i> BUFFER- PROTEIN	<i>D</i> (<i>R' - R</i>)	ΔD	$\left(\frac{\Delta C}{\Delta D}\right)$	$\frac{\Delta C}{\Delta pH}$
	<i>ohms</i>	<i>ohms</i>	<i>ohms</i>			
4.2	591.1	1113.0	521.9			
				12.9	0.07751	0.03875
4.4	562.0	1071.0	509.0			
				30.0	0.03333	0.01666
4.6	531.0	1010.0	479.0			
				31.5	0.03174	0.01587
4.8	492.0	939.5	447.5			
				30.5	0.03277	0.01688
5.0	460.3	877.0	417.0			
				32.1	0.03115	0.01557
5.2	425.0	809.9	384.9			
				27.4	0.03650	0.01825
5.4	396.5	754.0	357.5			
				22.1	0.04524	0.02262
5.6	371.9	707.3	335.4			
				16.1	0.06211	0.03105
5.8	356.7	676.0	319.3			
				15.3	0.06536	0.03218
6.0	346.2	649.0	304.0			

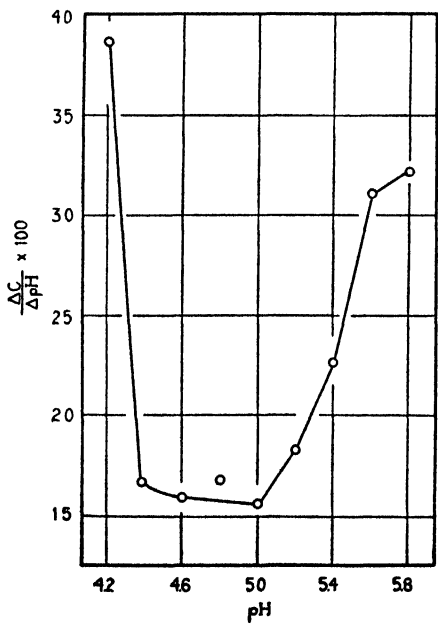


FIG. 4. Change in conductivity of glycine with change in pH

RESULTS

The data given in table 1 show clearly that the migration of the glycinin particles is at a minimum near a pH value of 5.02.

The minimum solubility occurs near a pH value of 5.02 (see table 2). The curve shown in figure 2 was obtained by plotting the pH as abscissa and the solubility expressed in milligrams per 50 ml. of solution as ordinate.

The data in regard to the viscosity of glycinin (table 3) show that the minimum time of flow occurred at a pH of 5.0. The curve obtained by plotting the time of flow in seconds against pH is shown in figure 3. The pH at which the protein shows a minimum time of flow is the same as the pH at which the protein shows its minimum viscosity. Therefore the minimum viscosity of the glycinin solution is near a pH value of 5.0.

The results of the conductivity measurements are given in table 4. R represents the resistance of the buffer solution alone, while R' is the resistance of the buffer-protein mixture. The resistance due to the protein is indicated by D . The term ΔD is the change in resistance due to a change in pH of 0.2; ΔC , the change of conductivity; and ΔpH the corresponding change of pH. The ratio, $\Delta C/\Delta pH$, represents the change in conductivity with respect to an accompanying change in pH.

According to the data in table 4 the value of the ratio $\Delta C/\Delta pH$ reaches a minimum when the pH is 5.00.

CONCLUSION AND DISCUSSION

It is clearly shown in the foregoing data that the isoelectric point of glycinin is near a pH value of 5.02 as determined by electrophoresis. Accordingly, the minimum physical properties, i.e., solubility, viscosity, and the ratio, $\Delta C/\Delta pH$, of the glycinin solution all occur at a pH of 5.0. The difference of pH in the isoelectric point as determined by electrophoresis and the pH of minimum physical properties is only 0.02. Thus, the data presented in this paper evidently confirm Loeb's statement (4), namely, that protein solutions show minimum physical properties at their isoelectric point. The difference of 0.02 in pH is no doubt within the limits of experimental error.

REFERENCES

- (1) CLARK, W. M.: Determination of Hydrogen Ions, 3rd edition, p. 200. Williams & Wilkins Co., Baltimore (1928).
- (2) JOHLIN, J. M.: Proc. Soc. Exptl. Biol. Med. **26**, 702 (1929).
- (3) KOCH, F. C., AND McMEEKIN, T. L.: J. Am. Chem. Soc. **46**, 2066 (1924).
- (4) LOEB, J.: Proteins and the Theory of Colloidal Behavior, 2nd edition, p. 10. McGraw-Hill Book Co., New York (1924).
- (5) MICHAELIS, L.: Die Wasserstoffionenkonzentration, p. 54, ff. 1. Williams & Wilkins Co., Baltimore (1926).
- (6) CHENG, L. T., AND HARTMAN, R. J.: Unpublished paper.
- (7) PEDERSEN, K. O.: Kolloid-Z. **63**, 268 (1933).
- (8) SHERMAN, H. C., THOMAS, A. W., AND CALDWELL, M. L.: J. Am. Chem. Soc. **46**, 1711 (1924).

THE APPARENT VOLUMES AND APPARENT COMPRESSIBILITIES OF SOLUTES IN SOLUTION. III

UNSATURATED AND SUPERSATURATED SOLUTIONS OF CALCIUM NITRATE

ARTHUR F. SCOTT AND G. L. BRIDGER

Department of Chemistry, The Rice Institute, Houston, Texas

Received October 17, 1935

The study of the effect of concentration on the apparent properties is, in the case of most electrolytes, limited to a relatively small range of concentration. Since there is no reason (5, 8) to expect the variation of solution properties to exhibit a discontinuity at the saturated state, one means of increasing the range of concentration is to consider the supersaturated state along with the unsaturated state. It was with this object in view that the present series of measurements of calcium nitrate solutions were undertaken. Highly supersaturated solutions of this salt, it will be recalled, are quite stable.

PURIFICATION OF MATERIALS

Water was doubly distilled, once from dilute alkaline permanganate, and once from dilute sulfuric acid through block-tin condensers.

Calcium nitrate was made by dissolving 1 kg. of technical calcium carbonate in an excess of c.p. nitric acid. After filtration to remove insoluble matter, the solution was made basic by adding pure calcium oxide in slight excess and again filtered to remove the insoluble magnesium hydroxide and most of the slightly soluble strontium and barium hydroxides. Further purification of the salt was accomplished by bringing about the crystallization of the tetrahydrate from a slightly acid solution, the crystals of which were collected and finally drained in the centrifuge. Two crops of the crystals, each roughly one-third of the material, were collected and the residual mother liquor discarded. The first crop gave negative tests for strontium, barium, and iron, and was used in making the first stock solution (No. 23). The second crop contained traces of strontium, barium, and iron. This portion of the salt was ultimately combined with solutions prepared from stock solution No. 23, and the crystallization process was repeated. The material obtained at this stage gave no further evidence of impurity and was used in making up stock solutions No. 20, No. 22, and No. 19. The calcium nitrate in the solutions prepared from these stock

solutions was again recovered by recrystallizing as the tetrahydrate and used to prepare stock solutions Nos. 18 and 21.

PREPARATION AND ANALYSIS OF SOLUTIONS

All of the solutions which were investigated were prepared by diluting or concentrating stock solutions. The solutions more dilute than the stock solutions were made by diluting weighed portions of the stock solution with water, the composition being obtained from the ratio of the weights before and after dilution. The supersaturated solutions were prepared by evaporating weighed amounts of the stock solutions in weighing flasks on the hot plate at about 70°C. During this operation the flasks were kept covered to prevent entrance of dust. When the solutions had evaporated to the desired composition, the flasks were stoppered, cooled, and weighed. Suitable counterpoises were used in all weighings and vacuum corrections were applied.

The analysis of four of these stock solutions was carried out by the following method, which is a modification of that described by Ewing (1). Enough solution to yield about 1 g. of anhydride was weighed in weighing bottles and evaporated in an electric oven at 110°C. overnight. The samples were then seeded with a minute particle of the anhydride and dehydrated to the anhydride by gradually raising the temperature to 170°C. Constant weight was usually attained in twenty-four hours, the samples being cooled in a desiccator over phosphorus pentoxide before weighing. In all cases triplicate determinations were made and vacuum corrections applied.

That this method of analysis is trustworthy and precise was shown by two sets of experiments which were carried out solely as checks. In one case, stock solution No. 20 was analyzed by the conventional oxalate method as well as by the dehydration method described above, giving the following values for the per cent of calcium nitrate:

<i>Analytical method</i>	<i>Mean of 3 analyses</i>	<i>Average deviation</i>
Oxalate \rightarrow CaO.....	53.65	0.10
Dehydration.....	53.40	0.02

In a second series of experiments, a solution was prepared by melting crystals of the tetrahydrate which had been dried in a vacuum desiccator over 60 per cent sulfuric acid (2). Analysis of this stock solution (No. 25) by the dehydration method gave 69.47 for the per cent of calcium nitrate, with an average deviation of 0.01. This mean figure is practically that (69.50 per cent) calculated from the formula of the tetrahydrate.

Toward the end of the work, when the high concentration region had been thoroughly investigated, three of the stock solutions were analyzed from density measurements. In order to have a sufficiently sensitive

means of determining the composition of these solutions from their density values, the following procedure was adopted. Using the data obtained from the four stock solutions analyzed by the dehydration method, a large scale plot of the ϕ (apparent molal volume) values against the corresponding density values was constructed. From this plot the ϕ values of the three new stock solutions could be read directly. With the ϕ value known, the composition of the solutions could then be calculated from the equation:

$$\text{Per cent Ca(NO}_3)_2 \text{ in the solution} = \frac{100M(v_w - v_s)}{Mv_w - \phi}$$

where

M = molecular weight of calcium nitrate,

v_w = specific volume of water = $\frac{1}{d_w}$, and

v_s = specific volume of solution = $\frac{1}{d_s}$.

This equation is a direct consequence of the definition of ϕ .

DETERMINATION OF DENSITIES AND COMPRESSIBILITY COEFFICIENTS

Three different sizes of pycnometers were employed for the determination of the densities of the calcium nitrate solutions. For all of the unsaturated solutions except Nos. 1, 2 and 4, the 100-ml. pycnometers described by Scott, Obenhaus, and Wilson (9) were used. In the case of the three exceptions just noted, the densities were determined with a 500-ml. pycnometer. Because of the difficulty of handling large amounts of the very viscous supersaturated solutions, a small 25-ml. pycnometer was employed in the density measurements of these solutions. Both the large and small pycnometers were of the same design as the 100-ml. pycnometers. It may be remarked here that, although the uncertainty in the density values is greater the smaller the volume of the pycnometer, the estimated uncertainty in the apparent molal properties turns out to be approximately constant for all concentrations.

The filling of the pycnometers with unsaturated solutions was carried out in the usual way. With supersaturated solutions the following procedure was found necessary. The solution was first warmed to about 70°C. in order to reduce the viscosity, and then drawn by suction into a pipet having a capillary stem. The solution in the pipet was then discharged slowly into the pycnometer by application of air pressure.

The apparatus and the procedure for the determination of the compressibility coefficients of the solutions have been described fully in previous papers (9, 10). It is interesting to observe that the glass piezometer has shown practically no change over a period of more than a year of con-

stant use. Thus, the value of the compression of the piezometer filled with mercury was redetermined and found to be 0.151 g. in place of 0.150 g., the former figure. Using this new value, the results of several new experiments yield for the compressibility coefficient of water 41.78×10^{-6} , a value which is essentially the same as the earlier value, 41.80×10^{-6} . In all calculations of the compressibility coefficients 4.00×10^{-6} has been accepted, as before, for the coefficient for mercury. In filling the piezometer with the supersaturated solutions, the method described above for filling the pyknometer was used. Since with the more concentrated solutions a greater period of time was required for the attainment of pressure equilibrium, a general practice was made in all measurements of taking the pressure reading 30 minutes after the initial application instead of after the customary 15 minutes.

EXPERIMENTAL RESULTS

The results of the experiments are summarized in table 1. The origin of each solution and the method whereby its composition was determined are indicated by the symbols in parentheses following the solution number. In this code "an" and "dens" signify that the solution was a stock solution and that the composition was determined by the dehydration or density procedure, respectively. Further, if the solution was prepared by concentration or dilution of a stock solution, say No. 23, this fact is shown by the symbols "c23" or "d23." All density values recorded in the table are the results of a single measurement. A majority of the compressibility coefficients are the mean values of duplicate measurements, the average deviations of which from the mean are given in the last column. The subscript digits in the last decimal place of some of the values indicate that the uncertainty may be as much as 3 or 4 units in that place.

DISCUSSION OF RESULTS

From the data given in table 1, values of ϕ (apparent molal volume), B (apparent molal compressibility), and $f \left[= \left(\frac{\partial \phi}{\partial c} \right)_p \frac{dc}{dp} \right]$ have been calculated by methods already described (10, 11) and are listed in table 2.

The relationships between the two apparent properties, ϕ and $(B + f)$, of calcium nitrate and the square root of the concentration of this electrolyte are portrayed in figure 1. The solid dots in this graph represent the values given in table 2 and the open circles represent ϕ - $c^{\frac{1}{2}}$ values at 18°C., which were calculated from data tabulated in the International Critical Tables. It should be noted perhaps that the quantities used in constructing the $(B + f)$ - $c^{\frac{1}{2}}$ plot are for solutions under a pressure of 200 metric atmospheres. The other two plots both portray solution data at atmospheric pressure. Attention is also called to the fact that at the top

of the graph a supplementary scale is marked which, corresponding to the bottom scale, shows the number of moles of water (n_w) per mole of solute in the more concentrated solutions.

With regard to the general nature of the ϕ - $c^{\frac{1}{2}}$ relationship, a question which has been the subject of numerous studies in recent years, two distinct views are held at present. According to Masson's empirical rule (6)

TABLE 1
Results of measurements on calcium nitrate solutions

SOLUTION NO	WEIGHT PER CENT	DENSITY AT 35°C	$\beta \times 10^6$ AT 35°C	AVERAGE DEVIATION
	0 00	0 994059	41 78	<0 01
1 (d21)	0 5282 ₀	0 99792 ₅		
2 (d21)	1 209 ₉	1 00291 ₇		
3 (d22)	4 114 ₇	1 0244 ₁		
4 (d21)	4 807 ₂	1 02966 ₀		
5 (d23)	7 337	1 0490 ₇		
6 (d22)	13 99 ₇	1 1027 ₄	36 40	0 02
7 (d10)	18 07 ₀	1 1376 ₂		
8 (d14)	19 90 ₃	1 1539 ₀		
9 (d23)	21 18 ₄	1 1656 ₇	33 51	
10 (d18)	23 54 ₈	1 1870 ₀		
11 (d19)	25 62 ₆	1 2066 ₃		
12 (d19)	26 63 ₂	1 2162 ₉		
13 (d18)	27 45 ₁	1 2241 ₄		
14 (d18)	28 57 ₁	1 2351 ₀		
15 (d23)	32 62 ₈	1 2763 ₇	29 31	0 04
16 (d18)	39 63 ₉	1 3510 ₈		
17 (d23)	47 01 ₀	1 4363 ₂	24 20	<0 01
18 (dens)	52 39	1 5028 ₉		
19 (an)	53 25	1 5138 ₈		
20 (an)	53 40	1 5160 ₀		
21 (dens)	53 44	1 5164 ₁		
22 (dens)	53 72	1 5200 ₆		
23 (an)	54 80	1 5339 ₁	21 70	0 01
24 (c23)	65 18	1 6772	18 83	0 04
25 (an)	69 47	1 7418		
26 (c20)	72 82	1 7941	16 78	
27 (c22)	75 23	1 8351		
28 (c22)	75 51	1 8392	16 06	

the ϕ - $c^{\frac{1}{2}}$ relationship for strong electrolytes is linear, the rate of change of ϕ with $c^{\frac{1}{2}}$ being markedly different for electrolytes of the same valence type. Theoretically also, as Redlich and Rosenfeld (7) have shown, this relationship in extremely dilute solutions should be linear, but the slope in this case is established by the valence type of the electrolyte. With these two conclusions in mind it is interesting to examine the ϕ - $c^{\frac{1}{2}}$ plot in figure 1. Since it is obvious that the plotted points do not fall on a straight

line, it must be concluded that solutions of calcium nitrate do not conform to Masson's rule. A similar, direct test of the theoretical deduction of Redlich and Rosenfeld is not possible, because our measurements do not extend into the region of extremely dilute solutions. It is worth noting, however, that the actual rate of variation of ϕ with $c^{\frac{1}{2}}$ in dilute solution is very much smaller than the theoretical value which is indicated in the graph. Furthermore, if, as is quite possible, the actual slope should

TABLE 2
Apparent molal properties of calcium nitrate solutions

SOLUTION NO.	c	c_{200}	ϕ	ϕ_{200}	$-\bar{B} \times 10^4$	$f \times 10^4$
	<i>moles/liter</i>	<i>moles/liter</i>	<i>ml.</i>	<i>ml.</i>		
1	0.0321209 ₀		44.1 ₄			
2	0.073944 ₈		44.6 ₄			
3	0.2568 ₈		46.2			
4	0.301632 ₀		46.3 ₆			
5	0.4690 ₈		47.1			
6	0.9405 ₉	0.9474 ₉	48.8 ₂	49.5 ₆	36.8 ₀	1.01
7	1.2527		49.8 ₀			
8	1.3995		50.2 ₀			
9	1.5048	1.5149	50.3 ₆	51.0 ₂	33.9 ₂	
10	1.7033		51.1 ₃			
11	1.884 ₄		51.5 ₆			
12	1.973 ₉		51.8 ₃			
13	2.047 ₈		52.0 ₆			
14	2.150 ₄		52.3 ₂			
15	2.537 ₉	2.552 ₉	53.1 ₆	53.7 ₀	26.9 ₃	1.99
16	3.263 ₆		55.0 ₃			
17	4.114 ₆	4.134 ₆	56.9 ₆	57.3 ₄	18.9 ₂	2.09
19	4.912 ₆		58.6 ₃			
20	4.933 ₃		58.6 ₄			
23	5.122 ₄	5.145 ₀	59.0 ₆	59.3 ₆	14.53	2.09
24	6.661 ₈	6.687 ₀	61.9 ₂	62.0 ₉	8.58	2.07
25	7.373 ₇		63.0 ₇			
26	7.961	7.988	63.9 ₉	64.0 ₈	4.66	2.02
27	8.413		64.5 ₂			
28	8.463	8.490	64.6 ₂	64.6 ₉	3.39	1.99

approach the theoretical slope as the concentration approaches zero, the complete ϕ - $c^{\frac{1}{2}}$ relationship would necessarily have a point of inflection in the region of dilute solution, a fact which would be indicative of a definite alteration in the structure of the solution state.

We have made two attempts to find a function which would represent the experimental data. The first possibility to be investigated was that ϕ is linearly dependent on c^x , where x has some other value than one-half, a relationship which Masson found to be valid for weak electrolytes and

non-electrolytes. The most satisfactory function of this kind may be written as follows:

$$\phi = 44.32 + 4.687c^{0.70} \quad (1)$$

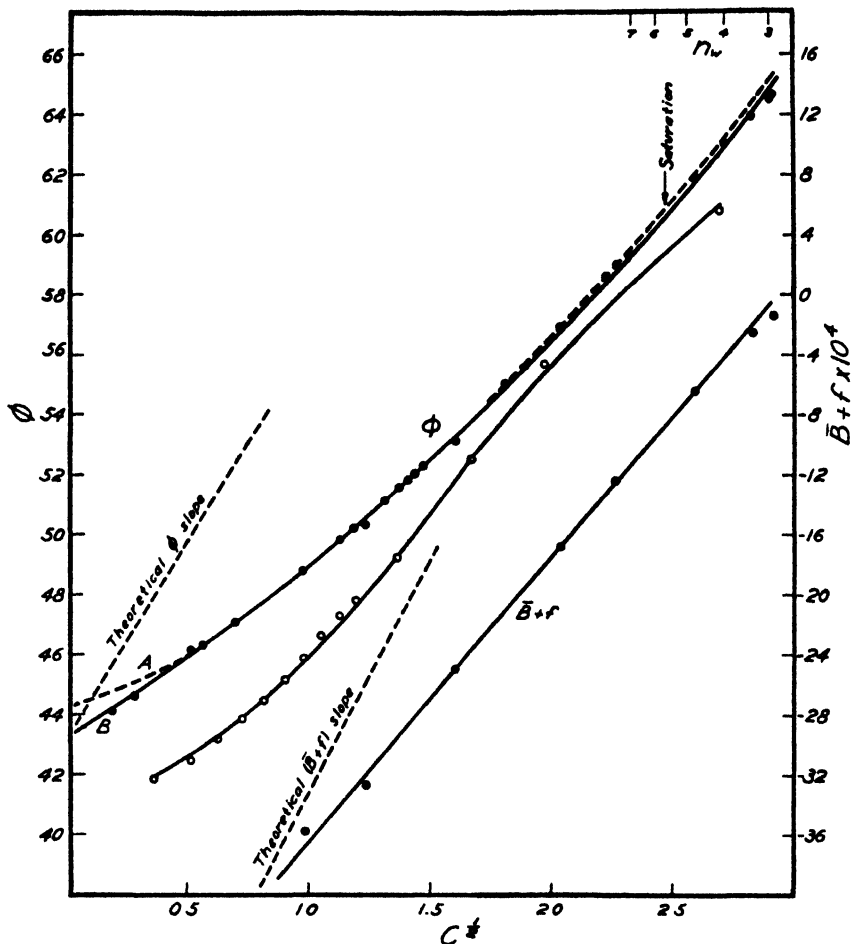


FIG. 1. Plots of apparent molal properties of calcium nitrate against the square root of the concentration. The two upper plots depict the apparent molal volume ϕ (left-hand ordinate) and the lower plot, the apparent molal compressibility $[\bar{B} + f]$ (right-hand ordinate).

Line A in figure 1 represents the values of ϕ , calculated from this equation, plotted against $c^{1/2}$. Although equation 1 appears to be reasonably satisfactory for a limited concentration range, it is by no means adequate for the entire concentration range covered by the experiments.

A second and more promising function is expressed by the following

equation, the constants of which were determined by the method of least squares:

$$\phi = 43.35 + 4.782c^{\frac{1}{2}} + 0.908c \quad (2)$$

Line B in the figure represents the variation of the calculated values of ϕ with changes in $c^{\frac{1}{2}}$. It may be noted that the average deviation between the calculated and experimental values of ϕ is slightly less than 0.1 ml., a quite satisfactory figure. A still better "fit" could be obtained if the data of the most uncertain solutions, those made from the first stock solution (No. 23), were neglected in the calculation of the constants of the equation.

Concerning the $(\bar{B} + f) - c^{\frac{1}{2}}$ plot in figure 1 only a few comments can be made. Because of the relatively large uncertainty in the plotted $(\bar{B} + f)$ values as well as the limited number of points available, no decision can be made as to the nature of the relationship between $(\bar{B} + f)$ and concentration. One possibility is that $(\bar{B} + f)$ is linearly dependent on $c^{\frac{1}{2}}$, the relationship indicated by the straight line drawn in the graph. The theoretical slope of this square-root relationship, as derived by Gucker (4) from considerations similar to those underlying the Redlich-Rosenfeld theory, is indicated in the graph. A second possible relationship is one analogous to equation 2, for if $(\bar{B} + f)$ values are plotted against the corresponding ϕ_{200} values, the plotted points, with the exception of those for the two most dilute solutions, fall closely on a straight line. The slope of this line $\frac{\partial(\bar{B} + f)}{\partial\phi_{200}}$ has the value 2.3×10^{-4} .

In concluding this discussion of the apparent properties of calcium nitrate in solution, it will be of interest to examine them further along lines which were developed in previous studies of the apparent properties of alkali halides in solution. First, it may be recalled that the maximum conceivable value of the apparent molal volume ϕ_m is reached, according to definition, when

$$\phi_m = \frac{1000}{c_m} \quad (3)$$

On the assumption that equation 2 is valid up to this limit of the solution state, the maximum value ϕ_m has been computed to be 73.5 ml. As was found to be the case with the alkali halides, this figure is a trifle larger than the molecular volume of the anhydrous salt, measurements of which range from 67.5 ml. to 73.4 ml. The maximum value of $(\bar{B} + f)$ corresponding to ϕ_m , assuming that these two quantities are linearly related, turns out to be 18.0×10^{-4} . The hypothetical value of the compressibility coefficient of the solute in this state is therefore $18.0 \times 10^{-4}/73.5 = 24.5 \times 10^{-6}$. This figure, by analogy with the corresponding quantities found with the

alkali halides, must be much greater than the compressibility coefficient of the solid anhydrous salt, the value of which has never been determined.

Another estimate of the compressibility coefficient, β_s , of the solid salt can be made, provided the relationship between $(\bar{B} + f)$ and ϕ_{200} is linear. Using the empirical rule, which was found to be valid for solutions of the alkali halides and which is expressed by equation 8 of paper No. I (10), β_s is calculated to be 12.4×10^{-6} . This estimate must be looked upon as somewhat too large. It is, for instance, approximately ten times greater than the compressibility coefficient of calcium carbonate. The failure to get a more reasonable value for β_s is due doubtless to the inapplicability of equation 8, mentioned above, rather than to a mistake in assuming a linear relationship between $(\bar{B} + f)$ and ϕ_{200} .

Finally, it may be noted that, although calcium nitrate in the solid state is known (3) in the forms of the di-, tri-, and tetra-hydrates, there is no definite evidence in the plots in figure 1 that these hydrates exist in the solution state. The fact that the ϕ and $(\bar{B} + f)$ values of the most concentrated solutions are low could be the consequence of a change in the solution state at a concentration corresponding to $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, the hydrate stable at 35°C ., but, because of the difficulty of working with the very viscous solutions, it is equally probable that the low values are due to errors in the measurements.

For the sake of completeness we may record the fact that the density at 35°C . of the crystalline tetrahydrate was found to be 1.896, which is essentially the same as the values (1.78 to 1.90) reported in the literature. Using this figure, the ϕ value is calculated to be 52.0 ml., which is 11.1 ml. lower than the ϕ value of the supercooled hydrate (solution No. 25). An attempt to determine the compressibility coefficient of the hydrated salt with our present piezometer was unsuccessful.

SUMMARY

Measurements of the densities and compressibility coefficients of both unsaturated and supersaturated solutions of calcium nitrate have been made at 35°C .

The effect of concentration on the apparent molal volume and compressibility of the solute is discussed. It is found that neither the empirical relationship of Masson nor the theoretical relationship of Redlich and Rosenfeld is applicable to these solutions.

REFERENCES

- (1) EWING: J. Am. Chem. Soc. **49**, 1963 (1927).
- (2) EWING: J. Am. Chem. Soc. **54**, 1335 (1932).
- (3) EWING, KREY, LAW, AND LANG: J. Am. Chem. Soc. **49**, 1958 (1927).
- (4) GUCKER: Chem. Rev. **8**, 111 (1933).
- (5) LIESEGANG: Scientia **57**, 345 (1935).

- (6) MASSON: *Phil. Mag.* [7] **8**, 218 (1929).
- (7) REDLICH AND ROSENFELD: *Z. physik. Chem.* **155**, 65 (1931).
- (8) ROTHMUND: *Löslichkeit und Löslichkeitsbeeinflussung*, p. 5. Verlag Barth, Leipzig (1907).
- (9) SCOTT, OBENHAUS, AND WILSON: *J. Phys. Chem.* **38**, 931 (1934).
- (10) SCOTT AND WILSON: *J. Phys. Chem.* **38**, 951 (1934).
- (11) SCOTT AND BRIDGER: *J. Phys. Chem.* **39**, 1031 (1935).

HIDE SUBSTANCE WITH HYDROGEN CHLORIDE AND AMMONIA

L. R. PARKS AND A. D. MELAVEN

*The Pond Chemical Laboratories, The Pennsylvania State College, State College,
Pennsylvania*

Received October 10, 1935

INTRODUCTION

In a study of the two-component system hide substance-hydrogen chloride, using the method of Bancroft and Barnett (1), Beck (2) reports that a compound is formed in which the combining weight of hide protein for hydrogen chloride is 332. The complete phase diagram was not obtained, but the compound was reported to have a dissociation pressure equivalent to 30 mm. of mercury at room temperature. Using the same method, Tsai and Hsiao (3) found that at 35°C., hydrogen chloride combines with hide protein to the extent of 26.4 mg. of HCl per gram of hide substance, to give the latter a combining weight of 1380. The dissociation pressure of this compound they reported as being equivalent to 1.41 mm. of mercury at 35°C. In the present work, complete phase rule data, obtained by the method of Bancroft and Barnett, are given for the two-component systems hide substance-hydrogen chloride and hide substance-ammonia. In neither case is there found to be any evidence of compound formation.

MATERIALS

The hide substance used was American Standard Hide Powder, obtained from the Standard Manufacturing Company of Ridgway, Pa., and was used without further treatment other than drying. The hydrogen chloride was generated by the action of c.p. sulfuric acid on crystalline ammonium chloride. It was dried by passing through two 4-in. columns of sulfuric acid before being added to the system. The ammonia gas was taken directly from a cylinder of anhydrous ammonia, obtained from the Matheson Company, North Bergen, N. J. The gas was passed through a 12-in. column of soda lime before being admitted to the reaction flask. The mercury was vacuum distilled before using.

METHOD

A weighed amount of hide powder was placed in a calibrated flask, which communicated with the gas supply through one arm of a mercury ma-

nometer connected directly to the reaction flask. After evacuation of the system, gas was added to the flask a few cubic centimeters at a time,

TABLE 1

Adsorption of hydrogen chloride by hide powder at low pressures

$$dp/dv = 0.96$$

HCl PRESENT AT 25°C. AND 760 MM. Hg	EQUILIBRIUM PRESSURE	HCl ADSORBED BY 5.0 G. OF HIDE POWDER	<i>x/m</i> IN MG. HCl PER GRAM OF HIDE POWDER
cc.	mm. Hg	cc.	mg.
9.6	0 012	9.6	2.86
29.9	0 04	29.9	8 90
60.8	0.10	60.7	18.1
76.7	0 15	76 6	22 8
98 5	0 36	98.1	29.2
124.4	0 48	123 9	36.9
165 0	1 20	163.7	48 8
203.5	2.20	201.2	60 0

TABLE 2

Adsorption of hydrogen chloride by hide powder

$$dp/dv = 1.24$$

HCl PRESENT AT 25°C. AND 760 MM. Hg	EQUILIBRIUM PRESSURE	HCl ADSORBED BY 5.0 G. OF HIDE POWDER	<i>x/m</i> IN MG. HCl PER GRAM OF HIDE POWDER
cc.	mm. Hg	cc.	mg.
177.2	1 5	176	52
295 3	7 8	289	86
312 7	9 5	305	91
349.3	11 5	340	102
374.6	15 6	362	108
400.7	19 5	385	115
459	34 8	431	128
554	68 2	499	149
709	150	588	175
819	208	651	194
942	300	700	209
1302	586	829	247
1371	649	848	253
1461	725	877	261
1298	555	850	253
1200	463	826	246
1074	343	798	238
934	224	754	225
793	122	695	207
693	70	637	190
573	32	547	163
401	9	394	117

waiting until the pressure reached a constant value before making further additions. The free gas remaining in the system at equilibrium was

calculated from the existing pressure and the previous calibration. Subtraction of this calculated value from the total amount of gas added gave the volume of gas taken up by the sample. By plotting the equilibrium pressure against the corresponding amounts of gas taken up by the sample, the phase diagram for the system gas-hide substance may be obtained. All pressure readings were made at 25°C.

Table 1 contains the data obtained for the system hydrogen chloride-hide substance, at low pressures. Table 2 contains the data for the same system over a greater range of pressure. Table 3 summarizes the data for the system ammonia-hide substance. The dp/dv values given in the

TABLE 3
Adsorption of ammonia by hide powder
 $dp/dv = 1.82$

NH ₃ PRESENT AT 25°C. AND 760 MM Hg	EQUILIBRIUM PRESSURE	NH ₃ ADSORBED BY 5.0 G. OF HIDE POWDER	x/m IN MG NH ₃ PER GRAM OF HIDE POWDER
cc.	mm. Hg	cc.	mg.
136	40	114	15.9
214.5	91	165	22.9
273	138	197	27.4
398.5	263	254	35.3
434	295	272	37.9
469	345	279	38.8
548	423	315	43.8
658	560	350	48.7
805	732	404	56.4
908	856	437	60.7
810	718	415	57.5
756	646	401	55.6
688	557	382	53.2
561	394	344	47.8
429	255	289	40.2
255.4	102.5	199	27.6
85.7	18.5	75.5	10.5
36.2	5.5	33.2	4.6

tables were obtained from the calibrations, and represent the change of pressure in the system, in millimeters of mercury per cubic centimeter of gas, measured at 25°C. and 760 mm. of mercury.

DISCUSSION

The phase rule, $P + V = C + 2$, where P represents the number of phases, V the number of degrees of freedom, and C the number of components, tells us that when a system of two components exists in three phases at constant temperature, the number of variables or degrees of freedom is zero. At constant temperature the pressure must remain

constant as long as three phases exist. On the phase diagram, the simultaneous existence of three phases is represented by a "flat," showing constant pressure, parallel to the axis of composition. The length of the flat, as measured on the composition axis, gives the ratio of the two components in the compound. When two components exist in but two phases at constant temperature, the number of degrees of freedom will be one, and the pressure will vary simultaneously with the composition. In this case a plot of the equilibrium data will result in a smooth curve. Phase diagrams constructed from the data of tables 1, 2, and 3 are of this type, showing that an adsorption complex rather than a true compound is formed.

An important factor to be considered in the construction of the phase diagram between hide substance and gases is that of equilibrium and the rate of its attainment. The disagreement of results in the present work with the results of Tsai and Hsiao and with the results of Beek is undoubtedly due to this factor. Tsai and Hsiao report that the equilibrium between hydrogen chloride and hide substance is established in one to two days. In the early course of this investigation it became apparent that a period of time considerably longer than one to two days was necessary for the system to arrive at the true equilibrium value. A period of twenty to twenty-five days was found in most cases necessary before readings that checked within the experimental error of the method were obtained. What has just been said applies in particular to the case where one proceeds from a lower to a higher pressure. In the reverse case, the hysteresis curves, obtained by proceeding from a higher to a lower pressure by removal of gas, represent values nearer the true equilibrium values, since check readings were usually obtained in fifteen to eighteen days after extraction. Since the pressure will decrease after addition of gas and increase after removal of gas, the conclusion is reached that the true equilibrium values lie between the two curves and are more nearly represented by the hysteresis or "down" curve than by the "up" curve. The experimental point at a pressure of 300 mm. and an x/m value of 209 may be used in support of this argument. This point is the value obtained after standing approximately twenty-five days. At this time it became necessary for the system to remain without further addition of gas for an additional period of time extending from July 14, 1933 to September 8, 1933, or approximately eight weeks. At the end of this time the pressure had fallen to a value of 287 mm. and the x/m value increased correspondingly to a value of 216. These values lie between the "up" and "down" curves.

The compound reported by Beek, whose vapor pressure was in the region of 30 mm. of mercury, had an equivalent weight of 332. This corresponds to 110 mg. of HCl per gram of hide substance. An examination of the

present work shows that the up curve gives an x/m value of 125 at 30 mm. of mercury, and the down curve, which probably represents a truer equilibrium value, gives an x/m value of 160 at the same pressure. Thus one must conclude that Beek's system had not reached equilibrium.

SUMMARY

Complete phase rule data, obtained by the method of Bancroft and Barnett, are given for the two-component systems hide substance-hydrogen chloride and hide substance-ammonia. An interpretation of these results indicates that adsorption complexes rather than definite chemical compounds are formed.

REFERENCES

- (1) BANCROFT, W. D., AND BARNETT, C. E.: J. Phys. Chem. **34**, 449 (1930). Phase rule studies on the proteins. I.
- (2) BEEK, J.: Bur. Standards J. Research **8**, 549 (1932). A contribution relative to the structure of collagen.
- (3) TSAI, L. S., AND HSIAO, C. J.: J. Chinese Chem. Soc. **2**, 87-98 (1934); Chem. Abstracts **28**, 6043 (1934); Chem. Zentr. **1**, 210 (1935). Adsorption of hydrogen chloride by hide powder.

AN HYPOTHESIS CONCERNING BACTERIOPHAGY

JOHN C. WILLIAMS

Department of Chemistry, Iowa State College, Ames, Iowa

Received October 11, 1935

A number of explanations have been advanced to account for bacteriophage and its action on bacteria. No evidence yet presented validates any one of these. D'Herelle considers phage to be animate, Wollman and Wollman (9) see a connection between it and the heredity of the organism, and Bronfenbrenner (2) believes it to be a stimulant of bacterial metabolism.

It is the purpose of this paper to propose and consider another hypothesis. It is suggested that phage may be a suspension of extremely small crystals of one or more of the compounds contained in the homologous bacteria. Bacteriophagy, then, would be the seeding of these amorphous compounds by the phage particle and their subsequent crystallization.

Evidence has been presented by a number of workers to show that phage is particulate; the size of the particles for various phages has been measured. That phage acts as an antigen indicates it is a protein, and Schlesinger's (8) analysis of a phage, in which he found 13 per cent nitrogen, confirms this. A number of proteins have been crystallized, so the hypothesis meets no difficulty here. Since proteins are hard to crystallize, it would be expected that spontaneous formation of crystals would be rare and that seeding would be highly specific; that is, only the appropriate crystal would start the amorphous compound crystallizing. Both of these conditions are in accord with the character of bacteriophage. A particular phage will attack only its homologous bacteria and closely related species. Furthermore, the spontaneous appearance of phage has been reported once or twice, although this has been generally ascribed to contamination. Plan-tureux (7) claimed to have prepared phage by what was essentially a crystallization method. He added graded amounts of calcium chloride solution to cultures of bacteria.

When bacteria are attacked by phage a number of cells simply disappear, while others swell until they burst. This is readily explained by the crystallization hypothesis. If the cell wall were damaged during crystallization, the contents of the cell would be discharged at once into the medium; if the cell wall retained its strength, swelling would follow. Con-

sider the interior of a cell in which crystallization had taken place. Synthesis would cease and, under the influence of the intracellular enzymes, chemical equilibrium would be restored. This would result in an increase in the number of molecules within the cell and water would be imbibed until the cell burst. In either case, the destruction of the cell would cause a dispersion of more crystalline material. Andrewes and Elford (1) have shown that if lysis is inhibited by sodium citrate, there is no increase in the amount of phage.

If bacteriophagy is crystallization caused by a seeding crystal, it should be sensitive to protective substances and to high viscosity. Bronfenbrenner and Hetler (3) have shown that the presence of 4 to 5 per cent agar in the medium inhibits bacteriophagy; Colvin (4) and Evans (6) have demonstrated that serum, ascitic fluid, saliva, pus, and urine have the same effect. D'Herelle (5) reported inactivation with glycerol.

The granular appearance of bacteria subject to bacteriophagy is perhaps an indication of crystallization.

D'Herelle (5) found bacteriophage to become more resistant to the action of deleterious physical and chemical agents during the first few days following its separation from susceptible bacteria. He interpreted this to mean that the smaller, less well fed parasites were the more resistant. On the basis of the present argument, it would be explained as the tendency of the larger crystals (which would grow at the expense of smaller ones) to keep their crystal structure longest under adverse conditions. The same applies to the gradual inactivation phage undergoes on standing.

If bacteriophage is the crystalline form of cell constituents, it should not have antigenicity independent of the homologous bacteria. Results of various investigators seem to show that it is an independent antigen. However, the procedures followed may not be decisive. If the bacterial antibodies are removed from the test serum by treating it with the whole bacteria, and the resulting serum gives a precipitation reaction with purified phage, the possibility remains that a compound within the cell was concerned, the antibodies for which would not have been removed. The antibodies should be removed with a suspension of disintegrated bacteria; if precipitation were still obtained from the phage-serum mixture, the hypothesis would be invalidated.

Inactivation of phage by serum should not be considered as evidence against the crystallization hypothesis; a crystal could be so coated as to be ineffective by traces of agglutinin which could not be removed from the serum.

My thanks are due to Dr. R. E. Buchanan and Dr. E. I. Fulmer for their careful consideration of this hypothesis.

REFERENCES

- (1) ANDREWES AND ELFORD: Brit. J. Exptl. Path. **14**, 367 (1933).
- (2) BRONFENBRENNER: J. Bact. **25**, 25 (1933).
- (3) BRONFENBRENNER AND HETLER: Proc. Soc. Exptl. Biol. Med. **30**, 1308 (1933).
- (4) COLVIN: J. Infect. Diseases **51**, 527 (1932).
- (5) d'HERELLE: Le Bacteriophage, Monographies de l'Institut Pasteur, p. 95 (1921).
- (6) EVANS: U. S. Pub. Health Repts. **48**, 411 (1933).
- (7) PLANTUREUX: Compt. rend. soc. biol. **103**, 387 (1930).
- (8) SCHLESINGER: Biochem. Z. **273**, 306 (1934).
- (9) WOLLMAN AND WOLLMAN: Ann. inst. Pasteur **49**, 41 (1932).

SPECIFIC HEATS AND RELATED PROPERTIES OF THE BINARY SYSTEM METHYL ALCOHOL-TOLUENE

L. S. MASON AND E. ROGER WASHBURN

Chemistry Laboratory, University of Nebraska, Lincoln, Nebraska

Received December 23, 1935

Departure of the behavior of binary liquid solutions from ideality has provoked a number of attempts to correlate measurements of physical constants with the state, and change of state, of molecular aggregation within the solution. The conclusions that may be drawn from a study of one type of constant, however, are often but partially sustained by, or wholly inconsistent with, those deduced from studies of some other constants. It is at present rather generally presumed that mutual solution of two or more liquids may be accompanied by dissociation of complex groups of molecules present in either or all of the component liquids into simpler units, and by aggregation of unlike molecules as a result of compound formation or the so-called process of solvation. Inconsistencies in the application of this view are attributed to variation in the sequence and degree in which the association, dissociation, and solvation occur as a result of the different thermodynamic conditions in which measurements of different constants are performed. The vagueness of such assumptions emphasizes the qualitative nature of our knowledge about these processes.

Various investigators have examined diverse phases of the problem of solution (2, 3, 4, 5, 6, 7, 10, 18). In this laboratory property-composition data are being accumulated for binary systems of low molecular weight alcohols with low molecular weight hydrocarbons of the aromatic series and with six-carbon cycloparaffins, and for ternary systems of the above combinations with water as the third component (11, 14, 15, 16). It is hoped that an extensive study of such systems will reveal more of the mechanism of solution than is at present known, and that results of such studies may afford generalizations more widely applicable than those in vogue.

During the course of these investigations interest in the pertinence of heats of mixing to the problems of solution has arisen. Knowledge of the specific heats of solutions is a prerequisite of the determinations of heats of mixing, and a study of the literature reveals but very few data on the specific heats of solutions of organic liquids. The purpose of the present work was to devise a convenient and efficient technique for determining

the specific heats of liquid mixtures and for measuring the heat changes attending the solution of the liquids, and to study these and other properties of the system methyl alcohol-toluene.

MATERIALS

Methyl alcohol. The methyl alcohol used was a synthetically prepared product of a degree of purity originally greater than 99.5 per cent. This alcohol was desiccated over lime and carefully fractionated in an all-glass still. The relative density of the purified product was $d_4^{25^\circ} = 0.78672$, and the refractive index was $n_D^{25^\circ} = 1.32659$.

Toluene. The best grade of toluene obtainable from the Eastman Kodak Company was treated repeatedly with freshly cut sodium and fractionated. No change in density was observed. A sample showed only a faint yellow coloration after standing over concentrated sulfuric acid for several hours. The relative density of the material was $d_4^{25^\circ} = 0.86229$ and its refractive index $n_D^{25^\circ} = 1.49365$. Toluene obtained from the Mallinckrodt Chemical Company was used for supplementary determinations of the thermal quantities after it had been treated with concentrated sulfuric acid, then sodium, and finally fractionated.

EXPERIMENTAL

Apparatus and procedure

Specific heats of solutions of methyl alcohol and toluene through the concentration range were measured adiabatically at 25°C. and 35°C. by a method involving the use of a Dewar flask in a hand-controlled air bath as a calorimeter. Heat was supplied to the liquids by a heating coil of nichrome wire of measured resistance, which was connected to two 6-volt storage batteries and a silver coulometer in series. The magnitude of the current passed was calculated from the weight of silver deposited in the coulometer and the length of time of deposition, the latter being measured with a stopwatch. The temperature rise was measured on a Beckmann thermometer which passed through a stopper fitting tightly in the Dewar flask. A series of five copper-constantan thermocouples indicated when any difference of temperature existed between the liquid in the flask and the air of the bath, and the bath was heated or cooled to restore equality of temperature. The heat supplied for each determination was calculated from Joule's law. All solutions for these and other measurements were prepared with weight pipets. The heat capacity of the calorimeter, which was found to be 20.86 cal. per degree at 25°C. and 21.41 at 35°C., was determined by using toluene and methyl alcohol as "standard" liquids in the calorimeter. The values are the averages of groups of determinations in which the average deviation from the mean is less than 0.7 per cent. The values used for the specific heats of methyl alcohol and toluene are those of Bose (1) and of

Williams and Daniels (17), respectively. The specific heats of methyl alcohol and toluene recalculated on the basis of the determined heat capacity of the calorimeter are 0.610 and 0.392 at 25°C. and 0.613 and 0.402 at 35°C.

The calorimeter was a Dewar flask of approximately 200-cc. capacity fitted with a cork stopper coated with water glass and equipped with a Beckmann thermometer graduated in 0.005°, a vertical glass stirrer, five thermocouples, and a nichrome heating coil. The series of thermal junctions was connected to a critically damped wall galvanometer whose deflections were observed with the customary arrangement of telescope and scale. The thermocouples were used only to indicate if a difference of temperature existed inside and outside the calorimeter. The resistance of the heating coil, which was found to be 7.730 ohms at 25°C., was measured potentiometrically by balancing the *IR* drop across the coil against the *IR* drop across a Bureau of Standards 10-ohm resistance. The temperature coefficient of the resistance of the heating coil exerted a negligible effect on the quantities measured at 35°C.

The air bath was a wooden cabinet 3 x 3 x 2 feet in dimensions, equipped with a window to permit observation of the interior, a large fan for circulating the air, and heating and cooling units which permitted rapid adjustment of the temperature of the interior to any desired value. A long metal shaft, attached eccentrically to a pulley above, passed through the roof of the cabinet and operated the stirrer in the calorimeter. The Beckmann thermometer in the calorimeter was read through the window of the cabinet by means of the telescope on a cathetometer.

The silver coulometer consisted of two electrodes of sheet silver, approximately 13 x 10 x 1 mm. in dimensions, supported by silver wires welded to them. These electrodes were suspended in a 1-l. beaker filled with an electrolyte, prepared according to the method of Wartenburg and Schutza (12) and stirred by a rotary stirrer. The cathode was weighed, before and after each deposition, after it had been thoroughly washed with distilled water, dried in an electric oven at 125°C. for ten to fifteen minutes, and allowed to cool twenty minutes. The electrodes were interchanged after six depositions had been made on one of them. The silver coulometer proved to be convenient and reliable for measurements of current strength. A good quality stop-watch graduated in tenths of a second was used to measure the lengths of time that current passed in the circuit.

Heat changes of mixing were measured for the concentration range at 25°C. and 35°C., using the same calorimeter as for the measurements of specific heats. A small flask, also equipped with thermocouples, was suspended in the cabinet in such a manner that a weighed amount of one liquid could be delivered directly into the calorimeter to be mixed with a weighed amount of the other liquid. The entire system was closed and

in temperature equilibrium before mixing. Temperature changes occurred within one minute, and it was found unnecessary to maintain adiabaticity during such a short time interval. It was necessary, however, to determine the heat capacity of the calorimeter for this short interval of temperature change. The value 16.9 cal. per degree was used for calculations at 25°C. and 17.6 at 35°C.

The densities of the series of solutions were determined at 25°C. and 35°C., using pycnometers of the type designed by Wade and Merriman (13). Volume changes were calculated from the measured densities.

TABLE 1
Specific heats

WEIGHT PER CENT ALCOHOL	WEIGHT OF SOLUTION	CATHODE WEIGHTS	TEMPERATURE RISE	TIME IN SECONDS	SPECIFIC HEAT
<i>T</i> = 25°C.					
10 17	84 440	0 2910	3 920	540	0 453
18 71	83 743	0 2974	3 996	540	0 474
28 37	83 025	0 2971	3 856	540	0 503
37 43	82.678	0 3065	4 083	540	0 518
52 27	81 452	0 3268	4 021	600	0 547
60 77	80 944	0 3310	4 058	600	0 564
70 94	79 991	0 3174	4 095	540	0 581
80 34	79 493	0 3028	3 873	510	0 600
89 55	79 041	0 3337	3 985	600	0 607
<i>T</i> = 35°C.					
9.17	85 030	0 3145	4.181	588	0 447
18.73	83 791	0 3063	3.913	576	0 479
28 09	83.273	0 3149	4.104	564	0 503
37 96	82 236	0 3124	4 044	552	0 525
47.66	81 608	0 3128	4 086	540	0 541
57.63	81.675	0 3034	3 833	528	0 560
68 21	80 555	0 3068	3 970	516	0 577
78 47	79.627	0 3048	3 951	504	0 597
89.25	78.231	0.3081	4 126	492	0 610

Refractive indices of the solutions were measured with reference to the D line of sodium at 25°C. and 35°C. with a Bausch and Lomb immersion type refractometer.

RESULTS

Some of the values obtained for the specific heats of the methyl alcohol-toluene solutions at 25°C. and 35°C. are given in table 1. The first column to the table, from left to right, expresses the weight per cent of alcohol in the solutions; the second, the weight of solution used in the determination;

the third, the weight of silver deposited in the cathode of the silver coulometer; the fourth, the temperature rise observed on the Beckmann thermometer; the fifth, the time in seconds during which the determination was performed; and the sixth, the calculated specific heat of the solution.

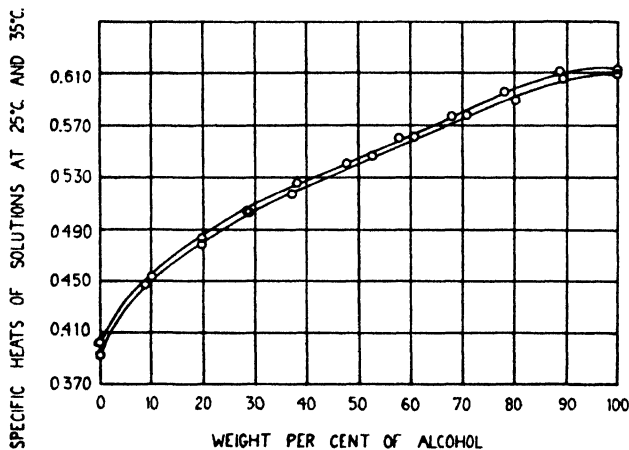


FIG. 1

TABLE 2

Changes in specific heat and partial molal specific heats

WEIGHT PER CENT ALCOHOL	C_p AT 25°C. FROM GRAPH	CALCULATED C_p AT 25°C	CHANGE OF C_p AT 25°C PER CENT OF CALCULATED C_p	C_p AT 35°C FROM GRAPH	CALCULATED C_p AT 35°C	CHANGE OF C_p AT 35°C PER CENT OF CALCULATED C_p	MOLAL C_p AT 25°C.	MOLAL C_p AT 35°C.	\bar{C}_p ALCOHOL AT 25°C.	\bar{C}_p TOLUENE AT 25°C.	\bar{C}_p ALCOHOL AT 35°C.	\bar{C}_p TOLUENE AT 35°C.
00 0	0 392	0 392		0 402	0 402		36 1	37 0				
10 0	0 448	0 414	+8 2	0 454	0 423	+7 3	34 7	35 2	31 1	36 3	29 8	37 3
20 0	0 481	0 436	+10 3	0 486	0 444	+9 5	32 2	32 6	28 7	36 7	27 6	37 6
30 0	0 504	0 457	+10 3	0 510	0 465	+9 7	29 7	30 1	25 1	37 8	25 0	38 4
40 0	0 524	0 479	+9 4	0 528	0 486	+8 6	27 6	27 8	22 8	39 0	22 9	39 6
50 0	0 541	0 501	+8 0	0 545	0 508	+7 3	25 7	25 9	21 4	40 1	21 7	40 5
60 0	0 559	0 523	+6 9	0 562	0 529	+6 2	24 2	24 4	20 5	41 2	20 5	42 0
70 0	0 576	0 545	+5 7	0 580	0 550	+5 5	22 9	23 1	20 4	41 5	20 4	42 2
80 0	0 592	0 566	+4 6	0 597	0 571	+4 6	21 8	22 0	20 3	41 7	20 3	42 2
90 0	0 604	0 588	+2 7	0 610	0 592	+3 0	20 7	20 9	20 1	43 0	20 1	43 2
100 0	0 610	0 610		0 613	0 613		19 5	19 6				

Duplicate determinations on solutions of the same concentration in all but a few cases vary less than 0.5 per cent.

Figure 1 is a graphical representation of the data shown in table 1. The upper curve shows the values obtained at 35°C. and the lower those at 25°C.

In table 2 the first column is the weight per cent of alcohol in the solutions; the second, the specific heat of the solution at 25°C. read from an enlarged graph like figure 1; the third, the specific heat of the solution

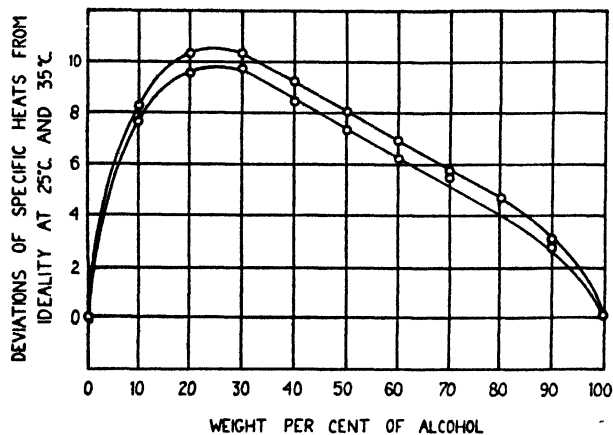


FIG. 2

TABLE 3
Heats of mixing

WEIGHT PER CENT ALCOHOL	WEIGHT OF MIXTURE	C_p OF MIXTURE	TEMPERATURE CHANGE	HEAT OF MIXING IN CAL. PER GRAM
$T = 25^\circ\text{C}.$				
10.38	86.067	0.450	-3.626	-2.343
19.62	84.592	0.480	-3.882	-2.639
29.80	85.299	0.504	-3.833	-2.692
38.82	81.922	0.521	-3.412	-2.482
48.28	80.930	0.538	-2.909	-2.174
57.64	81.214	0.554	-2.404	-1.832
68.07	80.395	0.573	-1.852	-1.450
78.56	78.999	0.590	-1.303	-1.047
88.68	79.046	0.602	-0.712	-0.581
$T = 35^\circ\text{C}.$				
10.10	85.223	0.455	-3.721	-2.462
18.86	84.023	0.483	-3.983	-2.758
37.74	82.032	0.523	-3.702	-2.731
57.74	81.150	0.559	-2.504	-1.943
78.61	79.337	0.595	-1.285	-1.050

calculated from a linear relationship; and the fourth, the deviation of the specific heat from the linear relationship expressed in per cent of the calculated specific heat (the + preceding the values indicates a positive deviation).

tion). The fifth, sixth, and seventh columns give the same values for 35°C. In the eighth and ninth columns are listed the molal specific heats of the solutions at 25°C. and 35°C., calculated by dividing the observed specific heat at each concentration by the sum of the number of moles of each constituent, assuming 1 g. of solution in all cases. In the last four columns are shown the partial molal specific heats, \bar{C}_p , of alcohol and toluene at 25°C. and 35°C., obtained by a graphical method described by Lewis and Randall (8).

In figure 2 the deviations of specific heats from ideality are plotted against the weight per cent of alcohol in the solutions at 25°C. and 35°C., the upper curve being for 35°C.

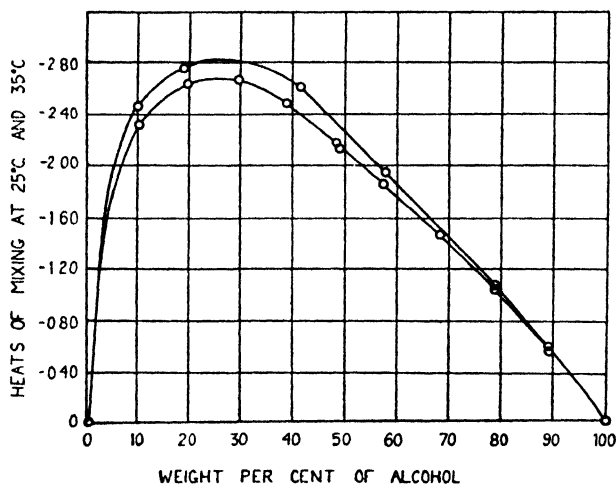


FIG. 3

Heats of mixing expressed in calories per gram of solution are tabulated in table 3, and are plotted against weight per cent of alcohol in figure 3. The upper curve represents the values at 35°C. The specific heats of the solutions used in the calculations were obtained from the graphs of the specific heats versus composition at the two temperatures.

In table 4 are found the observed densities and the volume contractions which attend mixing of the liquids at 25°C. and 35°C., together with the refractive indices and per cent deviations of refractive indices from a linear relationship for both temperatures. Volume changes are expressed in per cent of the volumes which the solutions would have had, had there been no change on mixing. Volume changes are plotted against concentration of alcohol in the solutions at both temperatures in figure 4. In these curves the greater deviations are observed at 25°C.

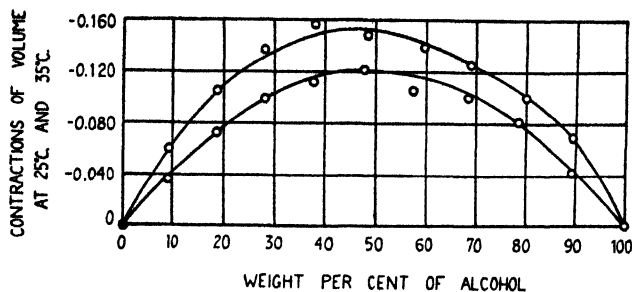


FIG. 4

TABLE 4

Changes in volume and refractive indices

WEIGHT PER CENT ALCOHOL	OBSERVED DENSITY	VOLUME CHANGE IN PER CENT	WEIGHT PER CENT ALCOHOL	OBSERVED REFRACTIVE INDEX	CHANGE IN REFRACTIVE INDEX IN PER CENT
<i>T = 25°C.</i>			<i>T = 25°C.</i>		
00 00	0 86229	000	00 00	1 49365	000
9 17	0 85528	-0 060	9 68	1 47622	-0 085
18 67	0 84799	-0 105	18 46	1 45903	-0 259
28 09	0 84081	-0 139	29 20	1 44120	-0 254
37 94	0 83330	-0 159	38 87	1 42523	-0 244
48 41	0 82519	-0 148	48 41	1 40873	-0 286
59 73	0 81666	-0 139	59 73	1 39045	-0 245
68 92	0 80977	-0 126	68 92	1 37544	-0 221
80 00	0 80156	-0 100	80 00	1 35756	-0 180
89 42	0 79463	-0 069	89 42	1 34289	-0 103
100 0	0 78672	000	100 0	1 32659	000
<i>T = 35°C.</i>			<i>T = 35°C.</i>		
00.00	0 85294	000	00 00	1 48839	000
9 17	0 84571	-0 036	9 17	1 47110	-0 151
18 67	0 83833	-0 072	18 67	1 45416	-0 242
28 09	0 83116	-0 106	28 09	1 43824	-0 280
37 94	0 82354	-0 112	37 94	1 42222	-0 273
47 66	0 81617	-0 122	47 66	1 40527	-0 333
57 54	0 80862	-0 105	57 54	1 38952	-0 308
67 97	0 80087	-0 097	67 97	1 37249	-0 310
78 47	0 79313	-0 081	78 47	1 35533	-0 300
89 25	0 78518	-0 042	89 25	1 33907	-0 192
100 0	0 77738	000	100 0	1 3240	000

DISCUSSION

If the heat added to solutions of methyl alcohol and toluene were utilized only for raising the temperature of the solutions, specific heat would be a straight-line function of composition, with the line terminating in the

specific heats of the pure components. The specific heats of the solutions, however, are greater than those calculated from additivity for all concentrations, as is shown by figure 1. Figure 2 emphasizes the extent of the deviations and shows the concentrations at which the deviations are most pronounced. Toluene is regarded as a normal liquid and methyl alcohol as strongly associated. The heating of solutions of the two liquids during specific heat determinations probably causes partial dissociation of the methyl alcohol, and this most markedly in the solutions of low alcoholic content. It appears that the presence of toluene enhances this dissociation by a dilution effect. The large heat capacities of the solutions of low alcohol concentrations are due, in a measure at least, to the absorption of heat involved in the process of dissociation of the alcohol aggregates. The plotted data indicate that the changes of specific heat from ideality are greater at 35°C. than at 25°C., which would suggest that a greater dissociation occurs at the higher temperature.

The partial molal heat capacities, \bar{C}_{ps} (values listed in table 2), are greater for all values calculated than the molal heat capacities of the pure liquids. Williams and Daniels (18) attribute such behavior to the formation of a compound of the components, or to the fact that heat capacity is increased by an increase in the number of molecules even though the total weight remains unchanged. It would seem that the latter effect is predominant in the system under consideration in view of the large negative heats of mixing, which furnish evidence that compound formation is unlikely. The difference between the partial molal heat capacity in solution and the molal heat capacity of the pure alcohol is greatest in the mixtures of low alcohol content, which would indicate a greater number of molecules and hence greater positive deviations from ideality for the heat capacities of the mixtures in that region of concentration.

The view that dissociation of the alcohol is aided by the dilution with toluene is supported by a consideration of the heat changes which attend solution of the liquids. At all concentrations, and at both 25°C. and 35°C., heat is absorbed on mixing, and the greatest absorptions are in the solutions of high concentrations of toluene, and these are greatest at 35°C. Evidence, in the case both of heat capacity deviations and of heats of mixing, indicates that more dissociation occurs at the higher temperature and at the lower concentrations of alcohol. It would be expected, however, that measurements at successively higher temperatures would ultimately show smaller and smaller deviations and smaller heat changes as the alcohol became more and more dissociated.

Large negative heats of mixing indicate the absence of compound formation or solvation in that these processes are usually associated with an evolution of heat. However, it is possible that such processes occur to a small extent, or with small evolution of heat, or conceivably, with a nega-

tive heat of formation. Under these conditions their thermal effects would be obscured by the heat absorption of dissociation.

It would be expected that an increase in the number of molecules in a solution, by virtue of dissociation, would be accompanied by an increase in volume, but in the case of the present system apparent dissociation of the alcohol is accompanied by a contraction in volume, and the largest contractions are found in approximately the same concentration areas as are the greatest deviations of specific heats and the greatest absorptions of heat on mixing. The evidence adduced from the thermal quantities indicates that dissociation is increased at the higher temperature, but volume contractions are found to be decreased. If a combination of alcohol and toluene molecules occurs in the manner suggested in connection with heats of mixing, the volume contractions might be reconciled. Such a combination, however, would be assumed to be quite unstable, and undoubtedly would be broken up when the temperature of the solutions was raised during determinations of heat capacities.

Washburn and Lightbody (15) observed that mixtures of ethyl alcohol with both benzene and toluene display both contractions and expansions of volume on mixing, and that methyl alcohol and benzene show both expansion and contraction. They postulated that a change from volume expansion to volume contraction is due to a shifting of the equilibrium among simple, complex, and compound molecules with changing concentration (9), but why methyl alcohol and toluene should be unique among these four systems in showing a contraction throughout the concentration range it is difficult to say, especially in view of the fact that the similarity of the liquids would lead to the expectation that the mixtures would behave similarly. Measurements of volume changes at other temperatures should be of help in answering this problem.

Refractive indices vary slightly from a straight-line function of composition, and the refractive indices of the mixtures are lower than the values obtained from calculations on the basis of an ideal solution. A decrease of refractive index is contrary to what would be expected if the only molecular change occurring in the solutions is one of dissociation of the alcohol. The supposed increased number of molecules together with a contraction in volume should produce an increase in the refractive indices. Here, as in the case of volume changes, a union of alcohol and toluene molecules may be the governing factor in causing the decrease in refractive indices. It would seem, however, that influences other than relative numbers of molecules are in effect, because the maximum deviations of refractive indices occur in solutions of greater alcohol content than do the greatest contractions in volume. Some changes in the chemical nature of the molecules, not yet understood, must be responsible for the situations observed. As yet it is possible to make only qualitative interpretations of the type of

data presented here, but more complete knowledge of this and similar systems should furnish evidence for roughly quantitative predictions.

SUMMARY

A rapid and efficient technique for measuring specific heats of solutions of organic liquids has been developed. The apparatus used, with slight modification, is readily applicable to the determination of heat changes attending solution of the liquids in each other.

Specific heats and heats of mixing of methyl alcohol-toluene solutions have been determined at 25°C. and 35°C. for the entire range of concentration. The heat capacities observed for the solutions are greater than those calculated from additivity for all concentrations. Mixing of the liquids is accompanied by an absorption of heat in all cases. Both effects are most pronounced in concentrations of low alcohol content.

The changes in volume resulting from mutual solution of the liquids, and the refractive indices of the solution, have been measured throughout the concentration range at 25°C. and 35°C. Solution of the liquids is accompanied by a contraction in volume; refractive indices are lower than those calculated on the basis of additivity.

The thermal effects observed are accounted for by assuming that methyl alcohol, which in the pure state is associated, undergoes dissociation into simpler molecular aggregates during mixing of the liquids and during subsequent heating in the determinations of the heat capacities of the solutions. A union of the constituent molecules has been assumed to explain the observed changes of volume and refractive index.

REFERENCES

- (1) BOSE, E.: *Z. physik. Chem.* **58**, 585 (1907). *International Critical Tables*, Vol. V, p. 114.
- (2) BRAMLEY, A.: *J. Chem. Soc.* **109**, 496 (1916).
- (3) BUSSY AND BUIGNET: *Ann. chim. phys.* **4**, 5 (1865).
- (4) DENISON, R. B.: *Trans. Faraday Soc.* **8**, 20 (1912).
- (5) DOLEZALEK, F.: *Z. physik. Chem.* **64**, 727 (1908).
- (6) HARTUNG, E. J.: *Trans. Faraday Soc.* **12**, 66 (1916).
- (7) KEYES, D. B., AND HILDEBRAND, J. H.: *J. Am. Chem. Soc.* **39**, 2126 (1917).
- (8) LEWIS, G. N., AND RANDALL, M.: *Thermodynamics and the Free Energy of Chemical Substances*, p. 38. The McGraw-Hill Book Co., New York (1923).
- (9) MADGIN, W. T., PEEL, J. B., AND BRISCOE, H. V. A.: *J. Chem. Soc.* **1927**, 2873.
- (10) PARKS, G. S., AND KELLEY, K. K.: *J. Phys. Chem.* **29**, 727 (1925).
- (11) VOLD, R., AND WASHBURN, E. R.: *J. Am. Chem. Soc.* **54**, 4217 (1932).
- (12) VON WARTENBURG, H., AND SCHUTZA, H.: *Z. Elektrochem.* **36**, 254 (1930).
- (13) WADE, J., AND MERRIMAN, R. W.: *J. Chem. Soc.* **101**, 2429 (1912).
- (14) WASHBURN, E. R., HNIZDA, V., AND VOLD, R.: *J. Am. Chem. Soc.* **53**, 3237 (1931).
- (15) WASHBURN, E. R., AND LIGHTBODY, A.: *J. Phys. Chem.* **34**, 2701 (1930).
- (16) WASHBURN, E. R., AND SPENCER, H. C.: *J. Am. Chem. Soc.* **56**, 361 (1934).
- (17) WILLIAMS, J. W., AND DANIELS, F.: *J. Am. Chem. Soc.* **46**, 903 (1924).
- (18) WILLIAMS, J. W., AND DANIELS, F.: *J. Am. Chem. Soc.* **47**, 1490 (1925).

MIXTURES OF COLLOIDAL ELECTROLYTES WITH UNI-UNIVALENT SALTS

JAMES W. MCBAIN AND JANET SEARLES

Department of Chemistry, Stanford University, California

Received November 8, 1935

Owing to the dearth of information as to the effect of mixtures of colloidal electrolytes and uni-univalent salts upon each other, the following data are instructive. One of the more interesting results of the study of colloidal electrolytes (1, 4, 5, 7, 9) is that the ionic strength principle does not apply to ionic micelles unless they are treated as uni-univalent electrolytes. Although ionic micelles are highly charged colloidal particles, their charges are spaced so far apart that they are effectively independent. In this respect, they are sharply differentiated from ordinary polyvalent ions in which the charges are coincident. The present data illustrate this in graphical form, both for freezing point lowering and for conductivity.

MODE OF CALCULATION

For comparison with the observed data for mixtures, it is customary to make use of various simple additive rules (2, 8, 10, 11). We have used three. First (method 1) is the "classical" mixture rule, where the molar conductivity, both observed and calculated, refers to the specific conductivity multiplied by the number of cubic centimeters containing one gram-equivalent of the common ion. For example, for mixtures of potassium laurate with potassium chloride

$$\mu_{\text{total K}^+} = \mu_{\text{KCl}_{\text{total}}} \times N_{\text{KCl}}/N_{\text{total}} + \mu_{\text{KL}_{\text{total}}} \times N_{\text{KL}}/N_{\text{total}}$$

where $\mu_{\text{KCl}_{\text{total}}}$ is the conductivity of a solution of potassium chloride alone of the same concentration of potassium ion as the total concentration in the mixture; whereas N_{KCl} is the actual equivalent weight normality (molality or gram-equivalents per 1000 grams of water) of the potassium chloride present. The assumption is that each salt contributes toward the total conductivity in proportion to its actual concentration and to its conductivity in a solution of the same total concentration as that of the mixture.

The second basis of comparison (method 2) is likewise only a first approximation to the truth, for it assumes that each salt present is exhibiting

the same conductivity in the mixture which it would have if the other salt were absent.

$$\mu_{\text{sum}} = N_{\text{KCl}} \times \mu_{\text{KCl}_N} + N_{\text{KL}} \times \mu_{\text{KL}_N}$$

This is compared with the observed conductivity of the mixture; that is, the observed specific conductivity multiplied by that volume which contains the stated number of equivalents of each of the two salts.

It should be noted that for solutions containing much soap, the values of weight normality and volume normality may differ by as much as 30 per cent, owing to the fact that soap solutions, in spite of the large weight of soap present, differ comparatively little in density from water. For this reason, application of the "classical" mixture rule to specific conductivities (method 3), that is, to equal volumes of solutions of the same total weight normality in common ion, leads again to a distinctly different result from the first method of comparison. All three provide some basis for examining the mutual effect of the constituents of the mixture. Data for pure substances were taken from International Critical Tables, published papers, or measured *ad hoc*.

Freezing points of mixtures were compared by two methods of calculation. The first (method 4) corresponds to the second of those above mentioned, that is, simple addition of the freezing points exhibited by each salt at a weight normality equal to that which it possessed in the mixture.

$$\theta_{\text{mixture}} = \theta_1 + \theta_2$$

Lastly (method 5), they were compared through the osmotic coefficient of the mixture

$$g_m = g_{1m} \times m_1/m + g_{2m} \times m_2/m$$

where g_{1m} is the osmotic coefficient of one constituent at the total molality of the mixture. Bjerrum's osmotic coefficient $g = 1 - j = \theta/v\lambda m$, where $v\lambda$ is the molal lowering at infinite dilution, obtained by diluting the mixture without changing the ratio between the two constituents. Thus

$$v = (v_1 m_1 + v_2 m_2)/(m_1 + m_2)$$

where $m = m_1 + m_2$ and $\lambda = 1.858^\circ$.

All conductivity data refer to $25.00^\circ \pm 0.01^\circ\text{C.}$, measured with the usual precautions in water of conductivity 0.5 to 1.0×10^{-6} in an oil thermostat. Freezing point measurements were by the Beckmann method with undercooling 0.3° to 0.5° . The best available materials were employed and all instruments were standardized.

The partial specific volumes of soaps above the concentration exhibiting minimum conductivity lie between 0.973 and 0.982 for lauryl- and myristyl-

sulfonic acids, and 0.945 to 0.935 for the *n*-undecylsulfonic acid; that for potassium laurate as found by Bury and Parry (3) lies between 0.912 and 0.917, but whereas the latter fell sharply in lower concentrations, the partial specific volumes of the straight chain sulfonic acids are slightly greater in more dilute solution.

CONDUCTIVITY RESULTS

Figure 1 exhibits the first two methods of comparison of mixtures of 0.955 N_w potassium laurate with potassium chloride up to 1.235 N_w . It is observed that the conductivity of the mixture by both methods of com-

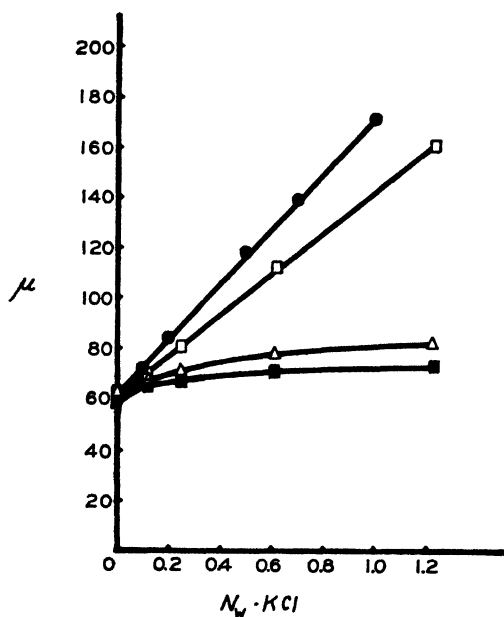


FIG. 1. Molar conductivity of 0.955 $N_w(m)$ potassium laurate containing potassium chloride. \blacksquare , observed, referred to 1 mole of total K; \triangle , sum of constituents (method 2); \square , observed, referred to total K in 1000 g. of water; \bullet , sum of constituents (method 1).

parison is definitely less than the calculated value. The same result follows from comparison of specific conductivities.

In contrast to this, figure 2, for mixtures of 0.1 N_w undecylsulfonic acid with hydrochloric acid up to 1 N_w , shows fairly close agreement between calculated and observed values, the latter being generally even higher. Similarly, if, according to the third method of calculation, observed conductivity is plotted against total molality (N_w) for true mixtures and separate constituents, the curve of observed values in every case lies slightly

but definitely higher even than the calculated values. This may be largely attributed to increased formation of ionic micelle.

A mixture, 0.1016 N_w with respect to laurylsulfonic acid and also with respect to hydrochloric acid, calculated by the first method, gave an equivalent conductivity with respect to total acid of 53.67 mhos as compared with the calculated value 54.6.

From the foregoing it may be concluded that the conductivity of the mixtures of soaps with electrolytes does not depart very much from simple additive rules.

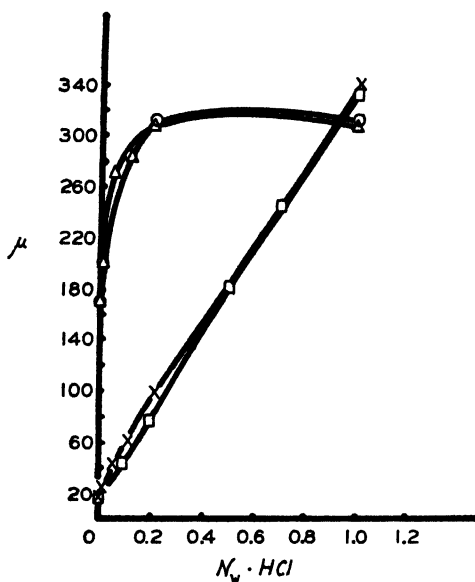


FIG. 2. Molar conductivity of 0.1 N_w undecylsulfonic acid containing hydrochloric acid. Δ , observed, referred to 1 mole of total H; \circ , sum of constituents (method 2); \times , observed, referred to total acid in 1000 g. of water; \square , sum of constituents (method 1).

FREEZING POINT RESULTS

Figure 3 exhibits the data for mixtures of 0.1 N_w undecylsulfonic acid with addition of hydrochloric acid up to 1 N_w . It will be seen that well within the error of experiment the total lowering is the sum of the constituents.

Figure 4 shows that the osmotic coefficient of the mixture is definitely even greater than that calculated from the constituents, for a mixture—0.1016 N_w laurylsulfonic acid containing 0.1016 N_w hydrochloric acid—exhibited a freezing point lowering of 0.440° , as compared with 0.420° for the sum of the constituents and an osmotic coefficient of 0.583 as com-

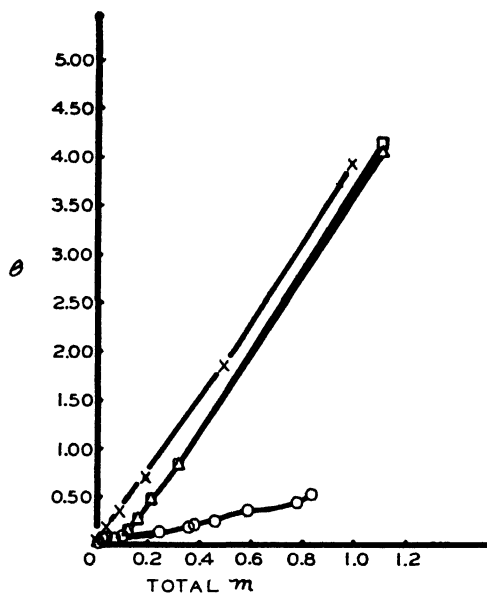


FIG. 3. Freezing point lowering (θ) of 0.1 N_w undecylsulfonic acid containing hydrochloric acid. \square , observed values; \triangle , calculated values (method 4); \times , International Critical Tables values for hydrochloric acid alone; \circ , Miss Betz' values for $C_{11}H_{23}SO_3H$ alone.

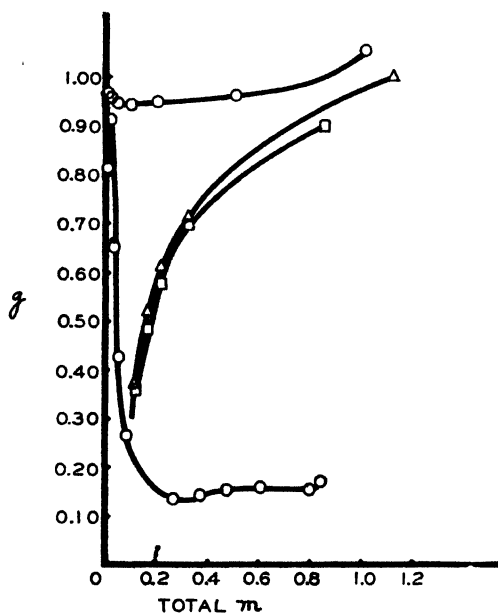


FIG. 4. Osmotic coefficients (ϕ) of 0.1 N_w undecylsulfonic acid containing hydrochloric acid. \triangle , observed values; \square , calculated values (method 5); \circ , International Critical Tables values for hydrochloric acid alone; \bullet , Miss Betz' values for $C_{11}H_{23}SO_3H$ alone.

pared with predicted 0.551. Thus again the observed values are higher than those calculated from the constituents. This result applies equally to ordinary soaps. Quick (6), for example, found the following dew point lowerings at 18°C.: 1 N_w potassium laurate, 0.22°; 1 N_w potassium chloride, 0.50°; mixture 1 N_w with respect to each, 0.77°, as compared with the sum of the constituents, only 0.72°. In these strong soap solutions, the increased lowering is presumably due to hydration of the soap.

It is evident that presence of ionic micelle does not exert any great effect toward suppression of conductivity or freezing point lowering as had been assumed by a number of writers.¹

Sodium salts of dibasic organic acids carry upon the anion charges which are far apart. The following mixtures were studied, concentration being expressed in molality, m ; the values of freezing point lowering in brackets are for the respective constituents, and the sum of these:—0.1 sodium chloride, 0.1 sodium oxalate (0.348°, 0.445°, 0.793°), 0.787°; 0.2 sodium chloride, 0.1 sodium oxalate (0.685°, 0.445°, 1.130°), 1.130°; 0.1 sodium chloride, 0.1 sodium succinate (0.348°, 0.532°, 0.880°), 0.885°; 0.2 sodium chloride, 0.1 sodium succinate (0.685°, 0.532°, 1.217°), 1.233°; 0.5 sodium chloride, 0.486 sodium succinate (1.675°, 2.545°, 4.220°), 4.305°; 0.1 sodium chloride, 0.1 sodium tartrate (0.348°, 0.476°, 0.824°), 0.803°; 0.2 sodium chloride, 0.1 sodium tartrate (0.685°, 0.476°, 1.161°), 1.141°; 0.5 sodium chloride, 0.5 sodium tartrate (1.675°, 2.002°, 3.677°), 3.626°; 0.230 sodium chloride, 0.115 sodium phthalate (0.775°, 0.731°, 1.506°), 1.475°; 0.5 sodium chloride, 0.247 sodium phthalate (1.675°, 1.561°, 3.236°), 3.510°; 0.270 sodium chloride, 0.137 sodium isophthalate (0.925°, 1.400°, 2.325°), 2.450°; 0.5 sodium chloride, 0.266 sodium isophthalate (1.675°, 2.814°, 4.489°), 4.464°; 0.230 sodium chloride, 0.113 sodium terephthalate (0.775°, 0.780°, 1.555°), 1.633°; 0.450 sodium chloride, 0.2315 sodium terephthalate (1.510°, 1.980°, 3.490°), 3.475°.

In every case it is seen that the observed lowering is, within experimental error, equal to that of the sum of the lowerings caused by the two constituents independently. For the tartrates, succinates, and *o*-phthalates, osmotic coefficients could be calculated and were likewise within a few per cent of those observed.

SUMMARY

Mixtures of ordinary electrolytes with ordinary alkali soaps or with hydrogen soaps, like mixtures of sodium chloride with sodium salts of organic acids, exhibit conductivities and freezing point lowerings in sub-

¹ G. W. Fuller in this laboratory has found that the electrometric titration curves of these hydrogen soaps show the normal form and position for a moderately strong univalent acid. A similar observation on gum arabic was made by Thomas and Murray (J. Phys. Chem. **32**, 696 (1928)).

stantial agreement with the simple additive mixture rules. In all these cases, the charges on the polyvalent ion or micelle are spaced so far apart as to be effectively independent. Hence the ionic strength of colloidal electrolytes resembles that for a uni-univalent electrolyte.

REFERENCES

- (1) BJERRUM, N.: *Z. physik. Chem.* **104**, 147; **106**, 219 (1923).
- (2) BRAY, W. C., AND HUNT, F. L.: *J. Am. Chem. Soc.* **33**, 781 (1911).
- (3) BURY, R. C., AND PARRY, G. A.: *J. Chem. Soc.* **1935**, 626.
- (4) MCBAIN, J. W.: *J. Am. Chem. Soc.* **50**, 1633 (1928).
- (5) MCBAIN, J. W., AND BETZ, M. D.: *J. Am. Chem. Soc.* **57**, 1912 (1935).
- (6) QUICK, W. C.: *J. Chem. Soc.* **127**, 1405 (1925).
- (7) SCATCHARD, G., AND KIRKWOOD, J. G.: *Physik. Z.* **33**, 297 (1932).
- (8) SHERRILL, M. S.: *J. Am. Chem. Soc.* **32**, 741 (1910).
- (9) SIMMS, H. S.: *J. Phys. Chem.* **32**, 1121 (for corroboration by Debye, see footnote 11, p. 1124), 1495 (1928); *J. Am. Chem. Soc.* **48**, 1244 (1926); *J. Gen. Physiol.* **11**, 613 (1928).
- (10) STEARN, A. E.: *J. Am. Chem. Soc.* **44**, 670 (1922).
- (11) VAN RYSSELBERGHE, P., AND NUTTING, L.: *J. Am. Chem. Soc.* **56**, 1435 (1934).

SIMPLE KINETIC THEORY OF IONIC EXCHANGE. I¹

IONS OF EQUAL VALENCY

HANS JENNY

Missouri Experiment Station, University of Missouri, Columbia, Missouri

Received October 17, 1935

INTRODUCTION

Many colloidal systems, particularly the aluminosilicates, the proteins, soaps, hydrous oxides, and numerous metallic colloids, exhibit the phenomenon of exchange adsorption or ionic exchange. Negatively charged colloidal particles are known to possess cation exchange (base exchange), whereas positive particles have anion exchange. Amphoteric colloids may comprise both types of reactions.

The present status of exchange adsorption is one of confusion. A great mass of experimental data is at hand, and over a dozen equations have been proposed. These are either wholly empirical or represent in the main questionable applications of the law of mass action. The constants of the equations have but little physical significance. No attempts have been made to advance a theory which links the exchange isotherms with other fundamental properties of colloidal systems such as electric potential and stability.

The purpose of the present study is to deduce on theoretical grounds an exchange adsorption isotherm. A very simple *ionic exchange model* will be depicted, and on the basis of kinetic concepts an equation will be formulated with the aid of statistical methods. Special emphasis will be laid on a rational interpretation of the constants. No claim is made that the model proposed and the equation deduced are valid for all ionic exchange systems known, but it is hoped that they will furnish a platform from which the great mass of empirical data may be viewed more intelligently than has been hitherto possible.

QUALITATIVE ASPECTS

Let us consider the special case of a large muscovite crystal. Upon being ground to colloidal dimensions the crystal breaks up, preferably along the basal cleavage planes. According to Pauling (4) these surfaces consist of layers of negative oxygen ions which form a rigid framework.

¹ Contribution No. 443, Journal Series of the Missouri Experiment Station.

Between the planes are located the potassium ions which, as a result of grinding, become exposed and appear in exchangeable form (figure 1). They behave as adsorbed ions, although previous to the mechanical treatment they were an integral part of the crystal. If the colloidal plates thus obtained are put into a solution of sodium chloride, ionic exchange takes place and a part of the potassium ions on the crystals is replaced by sodium ions. How shall such a surface reaction be pictured? It is important to remember that the potassium ions on the exposed oxygen layers are not at rest. Owing to heat motion and on account of the random

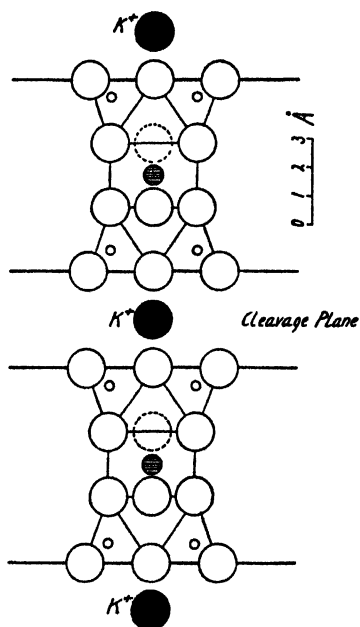
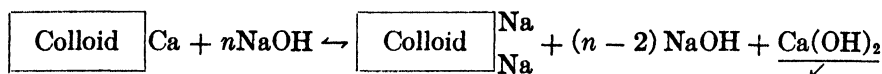
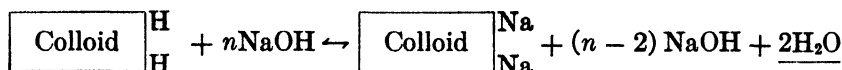


FIG. 1. Structure of muscovite according to Pauling (4). The large black circles are K ions; the large white circles are O and OH ions; the shaded small circles are Al ions in octahedra portions; and the small white circles are Al or Si ions within tetrahedra.

bombardment by water molecules, the potassium ions oscillate irregularly. At times they may be at a considerable distance (several Ångström units) from the wall, but are pulled back by the electrically charged oxygen ions. In the solution, the sodium ions wander at random as a necessary consequence of Brownian movement. Now, if it so happens that by chance a migrating sodium ion slips between the wall and an oscillating potassium ion which has momentarily moved away from the surface, an exchange reaction will occur. The positive sodium ion is electrically attracted by the negative wall, and the potassium ion is left in the solution or even

pushed into it by the electrical repulsion forces of the sodium ion. The chloride anion in the liquid does not participate in the reaction.

It should be emphasized that the mechanism proposed does not include the adsorption of cations or anions without an equivalent release of corresponding surface ions. Of course, weak electrolytes may be adsorbed as a molecular entity, but this case falls into the category of Langmuir's adsorption of molecules. In particular, the adsorption of OH ions, which is frequently reported in the literature, can be explained as mere anion exchange or a cation exchange involving hydrogen ions or polyvalent cations, according to the schemes:



In both cases OH ions may disappear from the solution, but not by means of straight adsorption. The subsequent increase in dispersion of the particles follows from the fact that Na-colloids have higher potentials than either H- or Ca-colloids (2).

For systems which do not contain bases (K, Ca, etc.) in the crystal lattice, for instance kaolinite, pyrophyllite, and many organic compounds, we believe that the OH ion of the crystal is the seat of exchange, or, more specifically, the H ion of the exposed OH ion will be replaced upon addition of an electrolyte.

QUANTITATIVE FORMULATION OF EXCHANGE ADSORPTION

We shall abandon the specific case of muscovite and work with the general case of a (planar) surface which contains a definite number of attraction spots per unit area. The ions, atoms, or molecules—or more generally the “particles”—which are initially adsorbed are called “black” or *b*. Those which are added to the system to function as exchanging particles are called “white” or *w*. Additional black particles which wander about like the white ones may also be introduced (corresponding to the special case of K-mica + NaCl + KCl). To simplify the mathematical treatment all particles are considered to possess the same mass and, if ions, the same electric charge but not necessarily the same size. The particles do not influence each other, and the principle of equipartition of energy is supposed to hold.

Terminology

Every adsorbed black particle oscillates within a given space called the oscillation cell, the average volume of which is v_b . The oscillation cell

is a very small fraction of the total volume (V) of the system. There are z_b attraction spots and consequently z_b adsorbed black particles on the entire surface. It shall be postulated that exchange occurs whenever a white particle enters an oscillation cell in such a way that it slips between the wall and the vibrating black particle or, more generally speaking, that it comes closer to the attraction spot. The number of white particles in V is N_w and the corresponding number of wandering black particles is N_b . The total number of b in V is therefore $N_b + z_b$. The average number of migrating w and b particles in one exchange cell (not counting the adsorbed ions) is

$$\mu = \frac{v_b}{V} (N_w + N_b)$$

which is the sum of:

$$\text{average number of } w \text{ in } v_b \text{ is } \frac{v_b}{V} N_w = \mu_w$$

$$\text{average number of } b \text{ in } v_b \text{ is } \frac{v_b}{V} N_b = \mu_b$$

The justification for using a simple statistical distribution instead of the Maxwell-Boltzmann principle lies in the nature of the exchange model suggested. Unlike the free surfaces operated with by Langmuir, Hückel, and others, the electric fields of the surface are "neutralized" by the adsorbed ions. Using the classical valence picture of the chemist, we assume that the attraction forces are localized in a straight line extending from the attraction spot on the wall to the center of the adsorbed ion. In other words, as long as the migrating ion does not come between the wall and the exchange ion—though it may be inside of the oscillation space—it is not under the influence of forces which differ from those in the bulk of the liquid. Furthermore, the adsorbed ions never evaporate, even in absence of migrating particles, otherwise the axiom of electroneutrality would be violated.

Distribution considerations

At any given instant some oscillation cells have no migration particles at all, some have one, others two, or three, or more. Again, those cells having one particle may have either a white one or a black one. The latter case would contribute nothing to the exchange process, since the replacement of a black particle by another black particle could not be detected experimentally. Cells with several particles may have all white, or all black, or mixtures of the two colors. The probabilities of these possible cases must be ascertained.

Let us designate the probability that a specific cell has none of the white particles by W_0 , that it has one white particle by W_1 , and in general, n particles of type w by W_n . Similarly for the migrating black particles we have B_0, B_1, \dots, B_n .

W_0B_0 is the probability that a given cell contains no migrating particles at all; W_1B_0 is the probability that it has a white particle, and W_0B_1 is the value for a wandering black particle. If two particles enter a specific cell the following cases exist:

Possibilities	Probabilities
$w\ w$	W_2B_0
$w\ b$	W_1B_1
$b\ b$	W_0B_2

For n particles we obtain the series:

$$W_nB_0 + W_{n-1}B_1 + W_{n-2}B_2 + \dots + W_0B_n = 1$$

According to definition only such cells will produce exchange as happen to have a white particle on the left of the oscillating b (figure 2); in other

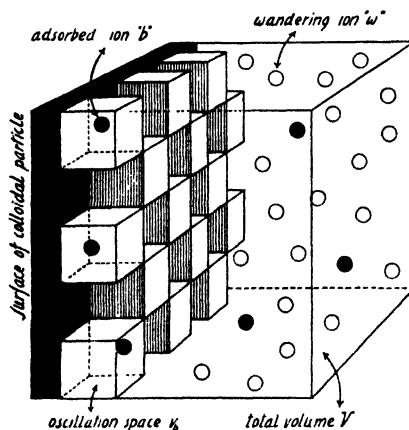


FIG. 2. Schematic representation of the surface of a plate of colloidal dimensions showing adsorbed ions (black) and their oscillation spaces

words, only a fraction of the cells with wandering w 's will actually show exchange. Designating the fractions by α_n, β_n, \dots , one obtains for the probability of exchange for n particles in a cell:

$$P_n = \alpha_n W_n B_0 + \beta_n W_{n-1} B_1 + \dots + \Omega_n W_0 B_n$$

The index n takes the successive values 0, 1, 2, 3, \dots . The total exchange probability, P , is the sum of these individual probabilities. For the sake of illustration the initial members of the final series shall be given:

$$P = \Sigma P_n = (\alpha_0 W_0 B_0) + (\alpha_1 W_1 B_0 + \beta_1 W_0 B_1) + (\alpha_2 W_2 B_0 + \beta_2 W_1 B_1 + \gamma_2 W_0 B_2) + \dots \quad (1)$$

Application of the Poisson series

The actual values of W_n and B_n in terms of v_b , V , N_w , and N_b are found with the aid of Smoluchowski's equations (5), also known as Poisson series:

$$W_{n(v_b)} = \frac{(\mu_w)^n}{n!} e^{-\mu_w} \quad \text{and} \quad B_{n(v_b)} = \frac{(\mu_b)^n}{n!} e^{-\mu_b} \quad (2, 3)$$

These equations yield the probability that n white or n black wandering particles are in a selected oscillation cell v_b .

Inserting equations 2 and 3 into formula 1 furnishes:

$$e^{-\frac{v_b}{V}(N_w+N_b)} \left[\alpha_0 + \frac{v_b}{V} (\alpha_1 N_w + \beta_1 N_b) + \left(\frac{v_b}{V} \right)^2 \left(\alpha_2 N_w^2 + \beta_2 N_w N_b + \gamma N_b^2 \right) + \dots \right] \quad (4)$$

In order to simplify the above expression, we shall conduct the experiments in such a way that V is very great in comparison to v_b , that is, use dilute sols only. The magnitudes of $\left(\frac{v_b}{V} \right)^n$ for $n > 1$ become very small in comparison to $\frac{v_b}{V}$, and the members with the higher terms of n in $\left(\frac{v_b}{V} \right)$ can be neglected. Since α_0 and β_1 are zero by definition, expression 4 reduces to:

$$\alpha_1 \frac{v_b}{V} N_w e^{-\frac{v_b}{V}(N_w+N_b)} \quad (5)$$

which is the probability of exchange for one cell under the experimental restrictions specified. For z_b cells the most probable number that will contribute to exchange is z_b times the above value.

The amount of exchange in the time Δt is a function of the velocity u of the particles. The rate of adsorption of white particles is evidently

$$\frac{\Delta w}{\Delta t} = z_b \alpha_1 \frac{v_b}{V} N_w e^{-\frac{v_b}{V}(N_w+N_b)} f(u) \quad (6)$$

which is also the rate of release of adsorbed black particles.

Equilibrium aspects

Equation 6 describes but one phase of the exchange phenomenon, namely, the release of black particles by white ones. The latter, which become adsorbed, may in turn be replaced by wandering black particles. The derivation of the equation of this reversed process is similar to the one just given, except that some of the symbols are to be changed: v_b

becomes v_w , the oscillation space of the adsorbed white particle, and z_b is changed to z_w , which represents the number of white particles adsorbed. The final equation corresponding to formula 6 is of the form

$$\frac{\Delta b}{\Delta t} = z_w \alpha_1 \frac{v_w}{V} N_b e^{-\frac{v_w}{V}(N_w + N_b)} f(u) \quad (7)$$

$\Delta b/\Delta t$ represents the rate of adsorption of black particles, which is also the rate of release of white particles. Equilibrium exists when

$$\frac{\Delta w}{\Delta t} = \frac{\Delta b}{\Delta t}$$

or

$$\frac{z_b}{z_w} \frac{N_w}{N_b} = \frac{v_w}{v_b} e^{\left(\frac{v_b - v_w}{V}\right)(N_w + N_b)} \quad (8)$$

Equation 8 is of a more general type than is required for the common base-exchange experiments. As a rule no wandering b particles are added to the migrating white particles. Furthermore, we shall express the equilibrium conditions in terms of white particles adsorbed (w_a) as a function of the white particles added (N_{w_0}). The following substitutions result:

$$\begin{aligned} N_w &\text{ becomes } N_{w_0} - w_a \\ z_b &\text{ becomes } z_{b_0} - w_a \\ z_w \text{ and } N_b &\text{ become } w_a \end{aligned}$$

Introducing these magnitudes into equation 8 leads to

$$\frac{(z_b - w_a)(N_{w_0} - w_a)}{w_a^2} = \frac{v_w}{v_b} e^{\left(\frac{v_b - v_w}{V}\right)N_{w_0}} \quad (9)$$

Inasmuch as v_b and v_w , and particularly $v_b - v_w$, are very small in comparison to V , the exponential term closely approaches 1; hence,

$$w_a^2 \left(1 - \frac{v_w}{v_b}\right) - w_a (z_{b_0} + N_{w_0}) + z_{b_0} N_{w_0} = 0 \quad (10)$$

For ordinary cation-exchange experiments we may write

$$\begin{aligned} w^2 \left(1 - \frac{v_w}{v_b}\right) - w(s + N) + sN &= 0 \\ + (s + N) \pm \sqrt{(s + N)^2 - 4sN \left(1 - \frac{v_w}{v_b}\right)} \\ w &= \frac{2 \left(1 - \frac{v_w}{v_b}\right)}{2 \left(1 - \frac{v_w}{v_b}\right)} \end{aligned} \quad (11)$$

where N = amount of electrolyte added initially (number of ions),
 w = number of cations adsorbed or released at equilibrium,
 s = saturation capacity, and

v_w, v_b = oscillation spaces of the adsorbed ions.

The equation has been deduced for a platy colloidal particle, but it applies to spheres as well; nor is it restricted to colloidal dimensions or to crystallites.

The most general equation embracing the case in which both white and black particles are added has the form:

$$w = \frac{\left[s + N_w + N_b \left(1 - \frac{v_w}{v_b} \right) \right] \pm \sqrt{\left[s + N_w + N_b \left(1 - \frac{v_w}{v_b} \right) \right]^2 - 4sN_w \left(1 - \frac{v_w}{v_b} \right)}}{2 \left(1 - \frac{v_w}{v_b} \right)} \quad (11a)$$

The symbols have the following meaning:

N_w = number of white particles added initially (electrolyte ion w),

N_b = number of black particles added initially (electrolyte ion b), and

w = number of white particles (electrolyte ion w) adsorbed or black particles (electrolyte ion b) released at equilibrium.

Equation 11a becomes of importance in studies on competition adsorption or competition exchange. Two kinds of particles, w and b , compete for a place on the surface. If N_b is zero, equation 11a goes over into equation 11. Figure 3 shows what types of curves can be expected in competition exchange. The uppermost curve depicts the conditions for $N_b = 0$, that is, no wandering black particles are added. If one introduces black particles equal to twice or ten times the saturation capacity ($N_b = 2S, 10S$), the adsorption of white particles becomes greatly repressed. This is most pronounced in low concentrations of the electrolyte ion w . The slope becomes less marked and the curves tend to approach straight lines. On the other hand, if equal numbers of white and black particles ($N_w = N_b$) are added, the slope of the curve becomes accentuated at low concentrations, whereas at higher concentrations the curve tends to run parallel to the abscissa, but never reaching the 50 per cent mark.

It is not likely that the natural colloidal systems are of such simple type that they correspond directly to the conditions which were specified for the ionic exchange model. A certain selection of the experimental results becomes necessary. Data obtained for very high electrolyte concentrations will have to be omitted in order to conform to the restrictions mentioned in the derivation of the equation. On the other hand, systems

of high dilution are apt to show disturbances due to hydrolysis effects, i.e., ionic exchange with hydrogen ions of water. Intermediate ranges of electrolyte concentrations appear to be most suitable to test the validity of the equation.

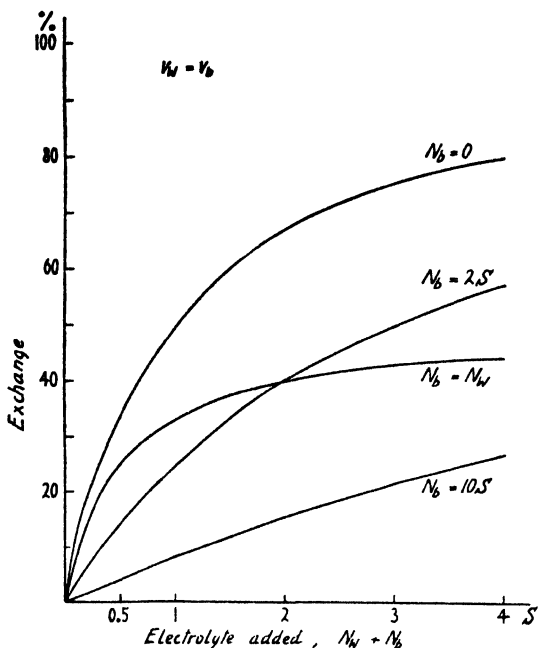
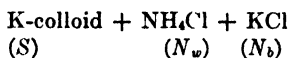


FIG. 3. Theoretical curves showing competition adsorption for a system of the type



The number of cations added is expressed in terms of saturation capacities (S). The intensity of exchange adsorption is given as per cent exchange in terms of saturation capacities. Activities are neglected.

Results with colloidal Putnam clay particles² (analyses by J. E. Gieseking)

The most careful and extensive work on ionic exchange has been carried out with aluminosilicates, and among these the permutites, zeolites, and natural soil colloids have been most extensively investigated. Cation-exchange experiments with purified Putnam clay were conducted according to methods previously described (1). In all experiments 7.5 g. of colloidal clay carrying 4.50 milliequivalents (M.E.) of adsorbed ions was treated

² The author is indebted to the National Research Council for a Grant-in-Aid.

with various amounts of chlorides, and the number of ions released was determined in the supernatant liquid. In every case the total volume of the system was 500 cc., and the temperature was kept constant at $28^{\circ} \pm 0.5^{\circ}\text{C}$. The exchange values expressed in terms of saturation capacities (4.50 M.E. = 100 per cent) are given in table 1 and also in figures 4, 5, and 6. The lines drawn were calculated with the aid of equation 11.

Upon inspection of the curves it must be concluded that the equation developed is able to describe very satisfactorily the position and trend of

TABLE 1
Ionic exchange experiments with Putnam clay
Analyses by J. E. Giesecking

SYSTEM	IONIC EXCHANGE PERCENTAGES FOR THE FOLLOWING INITIAL ELECTROLYTE CONCENTRATIONS 1 S = 4.50 M.E.				AVERAGE VALUE FOR $\frac{v_w}{v_b}$
	0.5 S	1.0 S	2.0 S	4.0 S	
NH ₄ -clay + LiCl	20.6*	29.9	44.4	54.7	5.16
NH ₄ -clay + NaCl	20.6	32.0	45.1	54.9	4.56
NH ₄ -clay + KCl	32.8	51.3	66.8	75.2	1.10
NH ₄ -clay + RbCl	41.1	62.6	80.2	90.0	0.354
NH ₄ -clay + CsCl	51.3	68.8	85.3	90.0	0.268
NH ₄ -clay + HCl	50.4	84.9	90.9	90.9	(0.03)
Ca-clay + MgCl ₂	32.1	47.5	63.3	76.7	1.23
Ca-clay + BaCl ₂	35.1	52.9	67.0	80.8	0.855
Mg-clay + BaCl ₂	28.7	50.3	71.0	83.6	0.800
H-clay + LiCl	4.5	6.6	9.0	13.0	207
H-clay + NaCl	3.5	6.2	9.8	13.5	197
H-clay + KCl	8.6	14.5	22.0	34.2	(31.4)
H-clay + RbCl	19.0	28.2	41.2	62.2	5.53
H-clay + CsCl	25.2	39.7	60.2	82.9	

* The first result indicates the following: There are 4.50 M.E. (1 S) adsorbed NH₄ (7.5 g. NH₄-clay) in 500 cc. volume and 1/2 S or 2.25 M.E. LiCl have been added. At equilibrium 0.927 M.E. NH₄ or 20.6 per cent have been released from the surface. The figure under "4 S" means that $4 \times 4.50 = 18.00$ M.E. LiCl have been added and 2.462 M.E. NH₄ or 54.7 per cent have been exchanged.

the curves over a considerable range of electrolyte concentration. In some instances the fitting is almost perfect; in others, systematic deviations seem to occur. They are especially noticeable in exchange reactions which involve hydrogen ions.

Influence of the structure of the colloids and the properties of the ions

Numerous exchange data published by various investigators have been tested as to the applicability of the equation, and the results lead to the following conclusions.

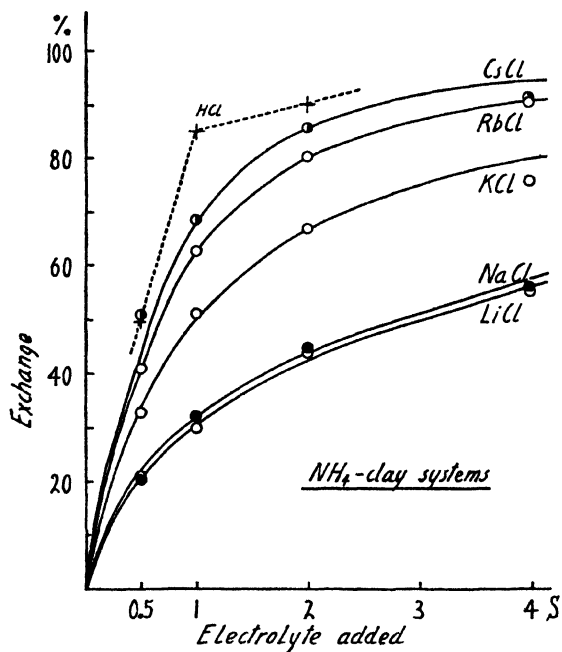


FIG. 4. Exchange isotherms for colloidal Putnam clay. Monovalent cations. Data are from table 1

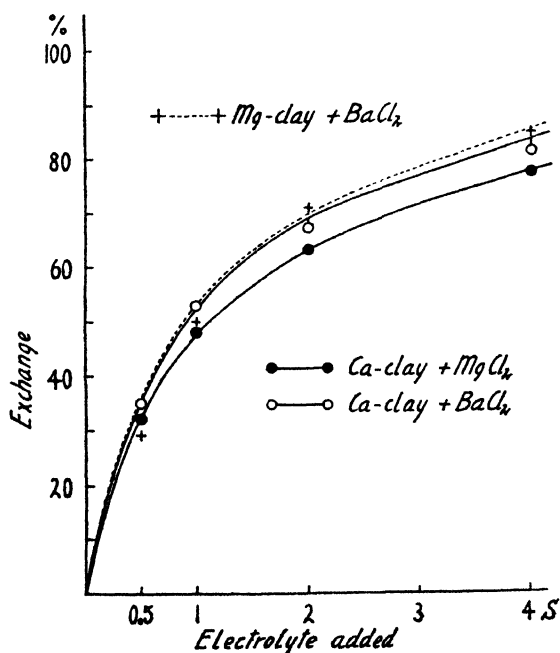


FIG. 5. Exchange isotherm for colloidal Putnam clay. Divalent ions. Data are from table 1

First, the *structure* of the colloidal particles appears to be an important factor. The equation yields good values for soil colloids and for bentonitic clays (data of Vanselow (6)), all of which have platy structures and seem to exchange on the outer surfaces only. Equation 11 is less satisfactory for permutites and certain zeolites. These systems are characterized by an abundance of ultramicroscopic pores and channels in which the exchangeable ions are seated. The ions are so close together that they interfere with each other, and by virtue of this fact the porous bodies fall outside of the realm of the equation.

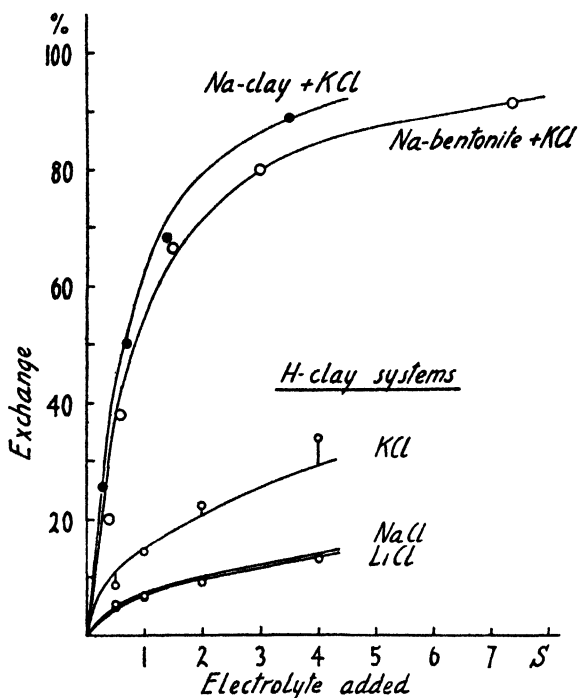


FIG. 6. Exchange isotherms for H-Putnam clay (table 1) and Na-clays and Na-bentonite. The two latter series are taken from Marshall (3)

Secondly, the *nature of the exchanging ions* has to be taken into consideration. If the ions differ greatly in their properties discrepancies occur. This is the case, for example, with the hydrogen ion as contrasted with the large size monovalent rare gas type ions (potassium, cesium), or barium versus magnesium. These can be explained as follows. The derivation of equation 11 rests on the assumption that the magnitude of the oscillation space is independent of the concentration of the wandering ions. However, according to Debye, the thickness of the ionic atmosphere of the electric double layer—which is related to the oscillation distance of

the adsorbed ions—varies as the square root of the electrolyte concentration. If the exchanging ions have similar properties, for example, size, then the ratio v_w/v_b is not affected by the number of migrating particles; however, in any other case the rates of change of v_w and v_b with salt concentration may differ materially from each other and the quotient v_w/v_b may vary with the electrolyte concentration; in other words, the constant ceases to be a constant. Refinements in the present mode of approach may ultimately overcome these difficulties.

Consequences of the base-exchange equation

Several investigators claim that ionic exchange involving ions of equal valency is not affected by dilution except for minor effects due to hydrolyses and changes in activities. Equation 11 agrees with this contention, inasmuch as it does not contain the magnitude V , that is, the total volume of the system.

Of particular interest is the behavior of the lyotropic series. According to figure 4 the adsorption series is of the form:

$\text{LiCl} \leq \text{NaCl} < \text{KCl} < \text{RbCl} < \text{CsCl} < \text{HCl}$ (exchange with NH_4 -clay)

and, as previously shown (1), the release series follows the reverse order: namely,

$\text{Li-clay} \geq \text{Na-clay} > \text{NH}_4\text{-clay} > \text{Rb-clay} > \text{Cs-clay} > \text{H-clay}$ (exchange with KCl)

Equation 11 predicts the latter series from the former as demonstrated in the following example. The system $\text{NH}_4\text{-clay} + \text{LiCl}$ yields the constant $k = v_{\text{Li}}/v_{\text{NH}_4}$, and consequently the ratio

$$\frac{1}{k} = k' = \frac{v_{\text{NH}_4}}{v_{\text{Li}}}$$

gives the desired constant for the reverse process, namely, $\text{Li-clay} + \text{NH}_4\text{Cl}$. This conclusion rests on the fact that the base-exchange equilibrium in many cases is a true one (for details compare Vanselow's hysteresis effect).

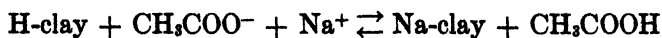
With the aid of equation 11 it is also possible to obtain information on exchange reactions which are difficult to study for analytical reasons, for instance the system $\text{Rb-clay} + \text{CsCl}$. If one determines $k_1 = v_{\text{Rb}}/v_{\text{NH}_4}$ from the system $\text{NH}_4\text{-clay} + \text{RbCl}$ and similarly $k_2 = v_{\text{Cs}}/v_{\text{NH}_4}$ from $\text{NH}_4\text{-clay} + \text{CsCl}$, the value

$$\frac{k_2}{k_1} = k_3 = \frac{v_{\text{Cs}}}{v_{\text{Rb}}}$$

furnishes the constant which is required to calculate the reaction $\text{Rb-clay} + \text{CsCl}$.

The average oscillation space v must be considered as a characteristic property of an adsorbed ion for a given colloidal particle. The common saying that "the ion b is better adsorbed than the ion w " simply means that b has a smaller oscillation volume than w , which implies that b is more strongly attracted by the surface.

Certain anions form undissociated compounds with the released ions, as illustrated by the reaction:



In such cases the equality $N_b = w_a$ no longer holds, and the equation given in the form of No. 11 cannot be applied.

Comparison with other adsorption equations

Equation 11 is of the same nature as the thermodynamic equation of Vanselow (6), except that his undetermined constant k has now a specific meaning, namely, the ratio of the oscillation spaces of the adsorbed ions. The solid solution or mixed crystal theory is unable to offer an explanation why the equation fails for certain systems such as permutites, zeolites, and H-colloids. The new equation possesses several advantages over the widely used Freundlich-Wiegner isotherm, because the constants have a distinct physical significance and the exchange is shown to reach a maximum. Moreover the Freundlich type of formulation does not include cases like K-colloid + NaCl + KCl. On the other hand the parabolic formula is somewhat more flexible because it contains an additional constant.

For ions of similar exchange intensities, such as NH_4 and K, the oscillation volumes assume equal magnitudes, $v_w = v_b$, and equation 11 reduces to

$$w = \frac{sN}{s + N}$$

which is identical in form with the Vageler-Langmuir exchange isotherm.

EXCHANGE ADSORPTION AND ELECTRIC POTENTIAL

v_w and v_b designate the oscillation spaces of the adsorbed ions in the absence of wandering ions. The cubic root of the ratio v_w/v_b is equal to the quotient of the average oscillation distances, that is,

$$\sqrt[3]{\frac{v_w}{v_b}} = \frac{\vartheta_w}{\vartheta_b}$$

The magnitudes ϑ_w and ϑ_b correspond to the thickness of the Helmholtz electric double layer of particles coated with w - or b -type ions. On the

basis of the diffuse double layer concept, ϑ is a measure of the distance from the wall to the electrical center of gravity.

The arrangement illustrated in figure 2 can be viewed from the standpoint of an electric plate condenser in which the negative plate is given by the rigid wall of negative oxygen ions and the positive plate by the

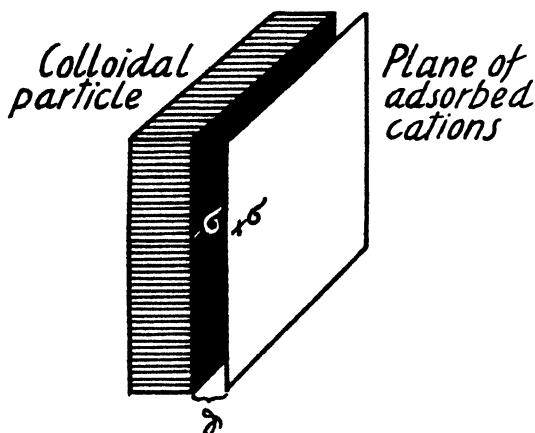


FIG. 7. Schematic presentation of a colloidal particle acting as an electric plate condenser. The black inner layer represents the wall composed of oxygen or hydroxide ions. The white outer layer represents a geometrical surface through the center of the average positions of the adsorbed ions.

average position of the cation coat (figure 7). The electric intensity between the plates is $4\pi\sigma/D$ and the potential difference is

$$P = \int_{\text{inner layer}}^{\text{outer layer}} \frac{4\pi\sigma}{D} d\vartheta$$

σ is the charge of the plates, which is equal to the saturation capacity of one particle, and D the dielectric constant. Thus we obtain ϑ_w for a colloidal particle with only ions of the w -type in the outer layer:

$$\vartheta_w = \frac{P_w D}{4\pi\sigma} ; \vartheta_b = \frac{P_b D}{4\pi\sigma}$$

and ϑ_b for a b -colloid. We arrive at the interesting equality

$$\frac{\vartheta_w}{\vartheta_b} = \frac{P_w}{P_b} = \sqrt[3]{\frac{v_w}{v_b}}$$

which shows that the ionic exchange constant is equal to the cube of the ratio of the potentials. The same relationship applies to large spherical

particles. In tables 2 and 3 are listed the experimental ratios based on measurements of potentials (2) of pure Ca-, Mg-, Li-, Na-, and other clays, and the base exchange constants from table 1. The agreement is satisfactory as far as the order of magnitude is concerned, and it is noteworthy that the position of the ions within the lyotropic series is strictly consistent in both sets of data. Numerous causes for the discrepancies could be cited; the major one is to be sought in the type of potentials actually measured. These are so-called zeta potentials, based on migration velocities of colloidal particles in electric fields, rather than the simple Helmholtz potentials. Furthermore it might be possible that the values

TABLE 2

Correlation between ionic exchange constants and electric potentials (divalent ions)

SYSTEM	$\sqrt[3]{v_w} : \sqrt[3]{v_b^*}$	$P_w : P_b^\dagger$
Ca-clay + $MgCl_2$	1.07	1.03
Ca-clay + $BaCl_2$	0.95	0.97
Mg-clay + $BaCl_2$	0.93	0.94

* From table 1.

† From reference 2.

TABLE 3

Correlation between ionic exchange constants and electric potential (monovalent ions)

P_b for NH_4 -clay = 56.0 millivolts

ION.....	Li	Na	K	NH_4	Rb	Cs	H
$\sqrt[3]{v_w} : \sqrt[3]{v_{NH_4}^*}$	1.73	1.66	1.03	1	0.71	0.65	0.31
$P_w : P_{NH_4}^\dagger$	1.05	1.03	1.01	1	0.98	0.96	0.86

* From table 1.

† From reference 2.

of the dielectric constants do not cancel but depend on the nature of the ion in the outer layer.

CONCLUSIONS

It appears that the ionic exchange mechanism proposed and the equation deduced permit a quantitative understanding of the most essential facts of exchange adsorption and its relation to problems of colloid stability (2). In some instances the agreement between theory and experiment is not so close as one might wish. Undoubtedly in the future the interaction of neighboring ions on and near the surface will have to be taken into consideration. Furthermore, the interpretation of electric potential measurements of colloidal particles needs elucidation.

SUMMARY

1. A simple model of the mechanism of ionic exchange has been proposed.
2. With the aid of the model an exchange adsorption isotherm has been theoretically deduced. The equation could be verified for colloidal clay systems over a considerable range of concentration.
3. Certain systems are but poorly governed by the equation. This particular behavior is explained on the basis of structural peculiarities of the colloidal particles and extreme variations of the properties of the participating ions.
4. The third root of the base exchange constant is shown to be equal to the ratio of the electric potentials of the double layers. This relationship directly connects ionic exchange with problems of colloid stability.

REFERENCES

- (1) JENNY, H.: *J. Phys. Chem.* **36**, 2217-58 (1932).
- (2) JENNY, H., AND REITEMEIER, R. F.: *J. Phys. Chem.* **39**, 593-604 (1935).
- (3) MARSHALL, C. E., AND GUPTA, R. S.: *J. Soc. Chem. Ind.* **52**, 433-43 (1933).
- (4) PAULING, L.: *Proc. Nat. Acad. Sci.* **16**, 123-9 (1930).
- (5) SMOLUCHOWSKI, M. V.: *Boltzmann Festschrift*, pp. 626-41, 1904.
- (6) VANSELOW, A. P. *Soil Sci.* **33**, 95-113 (1932).

THE REDUCTION OF SOME ADSORBED OXIDATION-REDUCTION INDICATORS

HAROLD A. ABRAMSON AND IVON R. TAYLOR

The Biological Laboratory, Cold Spring Harbor, New York

Received December 5, 1935

Although many oxidation processes in biological systems apparently take place at surfaces or in their presence, the study of oxidation-reduction reactions at phase boundaries in liquids does not seem to have been examined in simple systems. Furthermore, the analysis of the effects of an adsorbed substance capable of undergoing a reversible oxidation and reduction on the ζ -potential (electrokinetic potential) of inert and ionogenic surfaces may provide a new method of approach to the surface chemistry of oxidations and reductions. For these reasons we have investigated the effect of reductants on adsorbed methylene blue, litmus, and phenosafranine. It has been found that these dyestuffs can be reduced and reoxidized reversibly in the adsorbed state.

METHYLENE BLUE

Filter paper¹ was dipped into methylene blue solutions (about 0.5 per cent or more dilute) and the excess methylene blue washed off in running tap water, leaving the paper stained blue. If a piece of this blue paper is suspended in a stream of hydrogen in water or in phosphate buffer in the presence of platinized asbestos, reduction of the adsorbed methylene blue by the gaseous hydrogen does not occur to any appreciable extent.² The presence simultaneously of relatively large amounts of methylene white in solution complicates this result, because of the equilibrium set up between dissolved methylene white and adsorbed methylene blue. This was first observed by Doctor I. Korr in a preliminary experiment. Although hydrogen gas in the presence of large quantities of catalyst does not reduce adsorbed methylene blue, this can be readily brought about by addition of sodium hydrosulfite, cysteine, or thiourea. The thiourea, however, is efficacious only in acid solution. On addition of sodium hydrosulfite,

¹ Schleicher and Schüll No. 1. Also dye which has been adsorbed by blotting paper, adsorbent cotton, cotton toweling, porcelain, and hairs of a cleaning brush can be reversibly reduced.

² This confirms a personal communication to one of us (H. A. A.) from Professor L. Michaelis.

the slightly tinted solution of methylene blue becomes colorless, the filter paper itself then bleaching more slowly and in a spotty fashion but finally becoming white. If the white filter paper is now removed from the solution and the excess of reductant washed off, the paper remains white for some time unless the washing is prolonged. Most of the adsorbed methylene blue still remains on the filter paper in the form of methylene white, for addition of quinone or potassium ferricyanide restores the blue color to almost its original intensity. The adsorbed blue dye can now be reduced again and reoxidized several times. Cysteine does not reduce the adsorbed dye as quickly as hydrosulfite. Even with a 5 per cent solution of cysteine (Eastman Kodak) slight heating is needed for the reduction reaction to go to completion within a reasonably short time. With dilute solutions at room temperature the reduction may take hours. The auto-oxidation of adsorbed methylene white seems to take place readily in the air but rather slowly. As mentioned previously, traces of hydrosulfite or of cysteine adsorbed onto the filter paper inhibit the autooxidation of methylene white for a period quite sufficient to test the effects of other oxidants. Methylene white is known to be adsorbed by various surfaces. This can be demonstrated by dipping filter paper into a solution of methylene blue reduced by hydrosulfite or cysteine. After moderate washing in running water, little or no color appears. Addition of an oxidant however, reveals at once that a large quantity of methylene white has been adsorbed.

LITMUS

Litmus paper is rendered colorless by hydrosulfite in both acid and neutral solutions. Autooxidation is slow. The white paper can be washed in running water and then reoxidized to the red or blue dye depending on the pH.

PHENOSAFRANINE

This dye is readily adsorbed by filter paper and can be reversibly oxidized and reduced in the adsorbed state.

DISCUSSION

The bonds responsible for the adsorption of the dyestuffs here investigated do not appear to affect appreciably those groups involved in the oxidation-reduction process. A parallel instance is that observed for the ionization of adsorbed protein. Since the electric mobilities of protein-covered quartz particles do not differ very much from the dissolved protein, the free amino and carboxyl groups are not primarily involved in the adsorption reaction. It is of some interest to see a similar phenomenon occur with smaller molecules.

A surface having selective adsorption for one form of the constituents of

a reversible oxidation-reduction system could shift the oxidation-reduction potential of the system. Adsorption reactions of this type have apparently been investigated only with pH indicators. Thus Deutsch has shown that indicators like bromothymol blue, malachite green, and many others have the undissociated form of the dyestuff selectively adsorbed if adsorption occurs at a pH near the value of pK of the indicator. In this instance the pH of the solution does not change appreciably, for the color change occurs in well-buffered solutions. Since adsorbed methylene blue is not readily reduced by hydrogen gas-platinized asbestos, and since an electrode would indicate that the solution was very near the potential of the hydrogen electrode, it is evident that the electrometric measurement gives no indication of the potential at the surface (where adsorption occurs), even though the electrode potential has reached "equilibrium." In heterogeneous systems the attainment of "equilibrium" in solution does not necessarily indicate the reduction intensity at the surface. This should be borne in mind in connection with discussions involving the reduction intensity in living systems.

THE ADSORPTION OF THE HEAVIER RARE GASES BY MERCURY¹

HANS M. CASSEL AND KURT NEUGEBAUER

Department of Chemistry, Stanford University, California, and Technische Hochschule, Berlin, Germany

Received May 2, 1935

Since the nature of the van der Waals forces was revealed as a consequence of the atomic zero point vibrations of the electrons, the adsorption as caused by such attraction fields of solid or liquid surfaces also became accessible to advanced theoretical treatment. The theory due to London (12) at first was applied to the simplest example, that of spherical symmetrical atoms and molecules which may be regarded as spheres. Introducing certain further simplifying assumptions, London calculated the heats of adsorption by charcoal.

Owing to a numerical error, the values so obtained seemed at first to be in excellent agreement with the experimental results. The correctly calculated values, however, are only one-tenth, or, if repelling forces are disregarded, nearly one-fifth of the observed amounts. Thus, although the right order of magnitude is attained, there exists a discrepancy, the reason for which must be sought in the nature of the experimental conditions rather than in the theory.

As London has already pointed out, an increase of the attraction beyond that due to entirely plane surfaces is to be expected, owing to the porous structure of the crystalline adsorbent. Experimentally, it would seem possible to avoid these irregularities by using single crystals as the adsorbent. This method, however, has the disadvantage of so limiting the surface that it would be difficult to obtain measurable adsorption.

Measurement of the surface tension of liquid adsorbents may be a better procedure, for on this basis surface densities of the adsorbed gas atoms may be derived by the Gibbs thermodynamic equation. Though at first sight this method appears to be rather indirect, its advantage over the mere observation of adsorbed quantities is that it does not require a special measurement of the adsorbing surface area. The heats of adsorption are then derived from the determination of different isotherms.

¹ The measurements were carried out in collaboration with K. Neugebauer in the Technische Hochschule, Berlin; see also the dissertation of H. Binne, Technische Hochschule, Berlin, 1932.

Liquid mercury was used as the adsorbent in our experiments. This material proved to be well suited for checking the adsorption theory. Although in the earlier stage of our knowledge of the metallic state the application of London's theory to metals was objectionable, now, on the basis of Bloch's (2) ideas,² it is justified by the new dispersion theory of metals advocated by Kronig (9).

The experimental equipment was that previously used for the study of the adsorption of some polar and non-polar compounds by mercury (5) and was very similar to that of the capillary electrometer. In order to measure the surface tension, σ , the height of a mercury column necessary to press a mercury droplet through a small hole was determined. This opening, about 0.1 mm. in diameter, consisted of a stainless steel nozzle such as is employed for the purpose of manufacturing artificial silk. It was sealed to the bottom of a vertical glass tube communicating with the container of the mercury, which was purified by vacuum distillation and lifted pneumatically to the desired level. The observations made by means of a cathetometer were in error by less than 0.05 mm., that is to say, they corresponded to the formula

$$p = \sigma(1/r_1 + 1/r_2)$$

by less than 0.1 dyne per centimeter. In order to eliminate the uncertainty in the effective value of the curvatures, $1/r_1 + 1/r_2$, of the hole, the value 480.00 dynes per centimeter for the surface tension of mercury at room temperature (20°C.), as determined by Bircumshaw (1), was taken as a standard for calibration.³ Owing to the smallness of the radii, corrections for the influence of gravity could be neglected.

The accuracy of ± 0.05 dyne per centimeter thus obtained was, however, not sufficient to indicate any decrease of the surface tension by the action of argon at room temperature, even at a pressure of 100 mm. of mercury.

To continue the investigation, therefore, the heavier rare gases, krypton and xenon, were brought into contact with the metal. In these cases also the observable effects at room temperature were rather small, although well-defined values of the decrease in surface tension could be measured on cooling the system. Particular care was taken to keep the temperatures constant. Here of course the freezing point of mercury determined the lowest temperature.

The experimental results are given in the first and second columns of table 1. The corresponding figure (figure 1) shows the decrease in the surface tension, $\sigma_0 - \sigma = F$, as plotted against the gas pressure, p .

² We are indebted to Dr. Felix Bloch of Stanford University for his kind suggestions.

³ With the value recently obtained by Bradley (3) our results had to be increased by 4 per cent.

In the range of lower pressures, the isotherms are approximately straight lines converging towards the zero point. Under these conditions $dF/dp = F/p$, so that the Gibbs relation, $dF/dp = \Gamma RT/p$, yields the simple "two-dimensional" osmotic equation of state: $F = \Gamma RT$, where Γ denotes the number of adsorbed moles per unit area.

TABLE 1
Isotherms for adsorption of rare gases by mercury
a. Krypton

p	F	Γ	p	F	Γ
$T = 235^\circ\text{K.}$			$T = 253^\circ\text{K.}$		
mm Hg	dynes per cm.	10^{-12} cm^2	mm Hg	dynes per cm.	10^{-12} cm^2
93	0 35	1 1	60	0 20	0 6
198	0 85	2 5	160	0.50	1 6
263	1 10	3 4	221	0.75	2 2
320	1 30	4 0	339	1.15	3 4

b. Xenon

p	F	Γ	p	F	Γ
$T = 237^\circ\text{K.}$			$T = 253^\circ\text{K.}$		
mm Hg	dynes per cm.	10^{-12} cm^2	mm Hg	dynes per cm.	10^{-12} cm^2
50	1 65	5 0	59	1 20	3 5
89	2 85	8 5	130	2 60	7 5
198	6 05	18 0	234	4 40	12 0
331	9 10	25 0	295	5 50	15.5
Vapor density. 8 65			Vapor density 11.50		
Liquid density 43 50			Liquid density 52 50		
$T = 273^\circ\text{K.}$			$T = 293^\circ\text{K.}$		
69	0 80	2 0	40	0 35	1 0
93	1 10	3 0	91	0 70	2 0
146	1 75	4 5	149	1 20	3 0
227	2 75	7 5	205	1 60	4 0
278	3 35	9 0	280	2 00	5 5
Vapor density... 18 3			355	2 80	7 0
Liquid density. 47 7					

At higher pressures, the 237°K. and the 253°K. isotherm of xenon incline distinctly toward the p -axis. This curving, familiar from the Langmuir type of adsorption isotherms, in the case of mobile adatoms⁴ indicates a

⁴ The word "adatom," as introduced by F. A. Becker, is here used to designate the adsorbed particles according to Langmuir (10).

predominance of the virial term which arises from the repulsion of the adatoms over that due to the mutual attraction (6). Let us suppose that the simple van der Waals equation holds true for the gaseous state (constants a and b) as well as for the adsorbed state (constants α and β). The

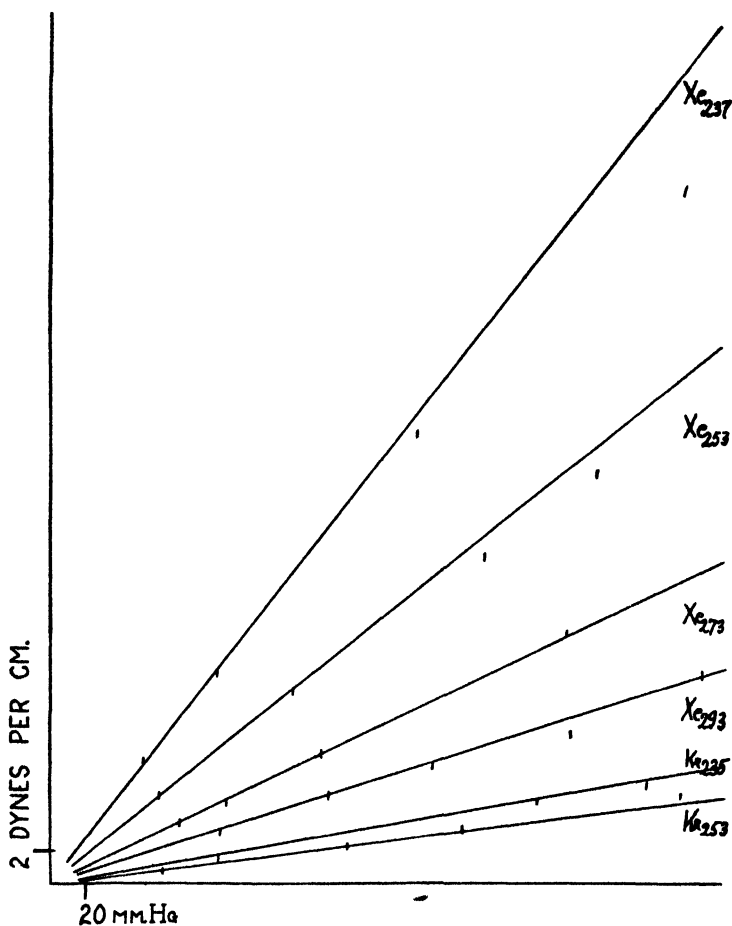


FIG. 1. The decrease of the surface tension, F , is plotted against the gas pressure. The observations are represented by vertical lines, the length of which corresponds to the possible error. The drawn straight lines are the initial tangents of the isotherms corresponding to the ideal two-dimensional gas law $F = \Gamma RT$.

critical temperature of the adsorbed state may then be estimated by means of the equation

$$T_{kads} = \frac{\alpha \cdot b}{a \cdot \beta} \cdot T_{kvol}$$

Since, according to Volmer (19), β is equal to twice the cross section of the adatoms, b/β is given by $8/3r$ if r denotes the radius of the atom. The amounts of a and α on the other hand, as determined by the virial coefficients of the attracting forces, may be calculated from the inverse seventh-power law as derived by London (12). Thus, the ratio a/α is found to be the same as b/β . Hence, in the case of xenon the critical temperatures should be equal, namely, 289.6°K. This deduction, however, fails to agree with the experiments.

The surface densities (number of atoms per unit area) of the liquid state and the coexisting vapor of xenon in bulk, as calculated from the measurements of Patterson, Cripps, and Gray (14), may be compared with the surface densities of the adatoms corresponding to the Gibbs equation as given in the third column of table 1. The values, although exceeding the vapor densities of 253°K. and 237°K., do not reach those of the liquid state.

It must be concluded, therefore, that the critical temperature of the adsorbed state lies below the range here observed. This behavior obviously corresponds to a very general rule (17): condensation phenomena in adsorbed layers occur only at temperatures far below the critical point of the masses in bulk.

In the case here studied, this may be due to the fact that the assumption of a free two-dimensional mobility is not quite justified, owing to distinct elementary spaces of adsorption. It was necessary to assume a semi-crystalline structure of the mercury, as was suggested for the interior of the liquid by Debye and Menke (8) and observed by Bresler (4) for the reflection of electron beams from the surface of liquid mercury. There is, furthermore, reason to believe that an increase in β beyond the value employed above could be brought about in the electric field of the metallic surface by the polarization, which reinforces the mutual repulsion of the adatoms by induced dipole moments.

For the purpose of further tests, the heats of adsorption on A , on the basis of the experimental results, were calculated for the different isotherms according to the formula (7),

$$A = RT^2 \left(\frac{\partial \ln p}{\partial T} \right)_r$$

which corresponds to the statement that the "dividing surface" coincides with the surface of the adsorbent. The values thus obtained are given in table 2.

The simplest method of checking these results, and one requiring a minimum of hypothesis, could be established by the knowledge of the binding energy, U , of the diatomic compounds between mercury and the rare gases. The existence of such molecules caused by polarization forces was suggested by Oldenberg (13) in order to account for his spectroscopical

observations. The heat of adsorption then may be calculated with satisfactory approximation, taking into consideration the attraction exerted only by the next neighbors of the adatom. This quantity, of course, depends on the type of arrangement of the atoms of the adsorbent. For hexagonal, spherical, close packing, corresponding to the work of Stranski and Kaischew (18), the inverse seventh-power law of attraction yields $A = 4.35 U$, as an average value of different possible surfaces (see table 3, A_d).

However, as the interpretation of the spectroscopic data is rather problematical, especially in the case of xenon, the complete requirement of the

TABLE 2
Heats of adsorption

GAS	TEMPERATURE	HEAT OF ADSORPTION
	$^{\circ}\text{K.}$	<i>cal.</i>
Krypton	239	2700
Xenon	245	3450
	263	3350
	283	3400

TABLE 3
Certain physical constants of the rare gases and mercury

ELEMENT	R_a	R_b	R_c	α	I	A_a	A_b	A_c	A_d	A_o	L
	<i>cm.</i> ⁻⁸	<i>cm.</i> ⁻⁸	<i>cm.</i> ⁻⁸	$\times 10^{-24}$	<i>kg-cal.</i>	<i>cal.</i>	<i>cal.</i>	<i>cal.</i>	<i>cal.</i>	<i>cal.</i>	<i>cal.</i>
Neon..	1 55	1 20	1.60	0 42	514	850	1200	800			(500)
Argon.....	1 85	1 47	1 95	1 70	375	2300	3250	2100	2700		1500
Krypton.....	1 95	1 57	1 98	2 35	332	2750	3900	2700	3700	3000	2300
Xenon.....	2 10	1 72	2 20	3 85	285	3750	5200	3500		3700	3100
Mercury...	1 60			11 2	240						

London theory has to be applied, representing the heat of adsorption by the equation:

$$A = \frac{\pi}{4} N \frac{\alpha\alpha'}{D^3} \frac{I \cdot I'}{I + I'}$$

where I and I' denote the ionization potentials, α and α' the atomic polarizabilities, N the number of mercury atoms per cubic centimeter, and D the distance of the adsorbate and the adsorbent, as given by the sum of the radii of the noble gas and the mercury atoms. Since this quantity enters with the third power, the results, of course, are greatly dependent upon the value chosen. The radius of the mercury atom was calculated

from the density of the crystal, assuming spherical close packing. Consequently the radii of the noble gas atoms were determined on the same basis, according to the work of Simon (16) and Ruhemann (R_a). To obtain an idea of the possible limits of variation, the amounts derived from the critical volume (R_b) and from the liquid densities (R_c) are also given in table 3, as well as the "spectroscopic" heats of adsorption (A_d), the heats of evaporation (L) (15), and the ionization potentials (I).

The heats of adsorption found experimentally had to be extrapolated to the absolute zero point. This was done upon the supposition that the specific heat of the adatoms equals that of the adsorbent (A_0).

While the agreement between theory and experiment was satisfactory for charcoal only as regards the order of magnitude, the observed values for mercury tend to coincide with the lower theoretical limit, which might have been expected since, as a first approximation, the forces of repulsion were disregarded.

SUMMARY

The surface tension of mercury in contact with krypton and xenon was measured at several temperatures and pressures. With the accuracy available (± 0.05 dyne per centimeter) the influence of argon could not be ascertained. The adsorbed quantities were calculated by means of the Gibbs equation, and the heats of adsorption derived from these isotherms were compared with the theoretical values according to the dispersion theory of the van der Waals forces.

We wish to express our thanks to Dr. Pollitzer, chief chemist of Linde's Eismaschinen, München, Germany, through whose kindness we obtained samples of the noble gases, and to Professor J. W. McBain of Stanford University for his kind interest.

REFERENCES

- (1) BIRCUMSHAW, L. L.: *Phil. Mag.* **12**, 596 (1931).
- (2) BLOCH, F.: *Z. Physik* **62**, 555 (1928).
- (3) BRADLEY, R. S.: *J. Phys. Chem.* **38**, 231 (1934).
- (4) BRESLER, S. E.: Unpublished work, information concerning which was contributed by Dr. J. W. McBain of Stanford University.
- (5) CASSEL, H., AND SALDITT, F.: *Z. physik. Chem.* **155A**, 321 (1931).
- (6) CASSEL, H., AND FORMSTECHE, M.: *Kolloid-Z.* **61**, 18 (1932).
- (7) CASSEL, H.: *Physik. Z.* **28**, 152 (1927).
- (8) DEBYE, P., AND MENKE, H.: *Physik. Z.* **31**, 797 (1930).
- (9) KRONIG, R. DE L.: *Proc. Roy. Soc. London* **133A**, 255 (1931).
- (10) LANGMUIR, I.: *J. Chem. Physics* **1**, 3 (1933).
- (11) LANGMUIR, I.: *Nobel Lecture*, 1933.
- (12) LONDON, F.: *Z. physik. Chem.* **11B**, 222 (1930).

- (13) OLDENBERG, O.: *Z. Physik* **55**, 1 (1929).
- (14) PATTERSON, H. S., CRIPPS, R. S., AND GRAY, R. H.: *Proc. Roy. Soc. London* **86A**, 579 (1912).
- (15) RABINOWITSCH, E.: *Abeggs Handbuch der anorganischen Chemie*, IV, 3 (1928).
- (16) RUHEMANN, B., AND SIMON, F.: *Z. physik. Chem.* **15B**, 389 (1932).
- (17) SEMENOFF, N.: *Z. physik. Chem.* **7B**, 471 (1930).
- (18) STRANSKI, I. N., AND KAISCHEW, R.: *Z. Krist.* **78**, 373 (1931).
- (19) VOLMER, M.: *Z. physik. Chem.* **115**, 253 (1925).

TIN VANADATE AS A CATALYST IN THE OXIDATION OF TOLUENE TO BENZOIC ACID¹

ROY HUITEMA AND O. W. BROWN

Department of Chemistry, Indiana University, Bloomington, Indiana

Received August 20, 1935

INTRODUCTION

It has been known for centuries that certain gums are capable of preventing decay. Some of these gums were used by the Egyptians in the preservation of their dead. It was found that the preserving action of these gums was due to benzoic acid, one of their constituents. The insects caught by some insectivorous plants are preserved for long periods of time by the benzoic acid excreted from the leaves of these plants. At the present time use is made of the preserving action of this acid and its salts in the treatment of certain foods to prevent spoilage. The acid and its salts also find some use in medicine as well as in the manufacture of certain dyes.

When the acid or its salt is to be used in medicine or for the preservation of foods, the presence of certain impurities is considered to be particularly harmful. Much of the acid produced from chlorinated toluene contains combined chlorine as an impurity. Since the removal of this material presents a difficult problem, some other method for preparing benzoic acid from toluene is being sought.

In 1875 Coquillion (2) found that toluene vapor could be oxidized to benzoic acid by air in the presence of certain catalysts. Weiss and Downs (7) have given a review of the literature on the subject of catalytic oxidations, along with a report concerning their own work in this field. One of the most outstanding researches on the catalytic oxidation of toluene is that of Maxted (6) in which he used a catalyst of tin vanadate.

Advantages of a vapor phase catalytic process for the preparation of benzoic acid from toluene are obvious. The product may be made to sublime from the reaction chamber in a comparatively pure state with no inorganic contamination. Air has a sufficiently high concentration of oxygen to bring about the desired reaction, providing other conditions are properly chosen. Since the reaction is exothermic, external heating of the

¹ This paper is based upon a thesis submitted to the Graduate School of Indiana University by Roy Huitema in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry, June, 1934.

apparatus should be unnecessary. Any by-products of the catalytic process for the oxidation of toluene should be of such a nature as to present no difficulty in their disposal.

Numerous patents have been granted covering the use of certain materials as the contact mass in the vapor phase catalytic oxidation of toluene and related compounds. The catalysts which find the greatest favor with the investigators are the compounds of vanadium. In fact many oxidations, both organic and inorganic, are catalyzed by compounds of this element. Although vanadium pentoxide was one of the compounds first used in this type of work, it has been supplanted to some degree by the vanadates. Since tin vanadate has been reported to be especially active in the oxidation of toluene to benzoic acid, it was thought advisable to investigate the behavior of this catalyst a little more closely.

THEORETICAL CONSIDERATIONS

Several possible reactions may take place in the oxidation of such a compound as toluene. The nature of the reactions and the extent to which they occur are determined largely by the following conditions: temperature of the reaction chamber, pressure, nature of the catalyst, nature and proportion of diluent gases, and the proportion of oxygen to toluene vapor.

From a technical point of view the question of greatest importance is that concerning the ratio of the quantity of toluene converted to the desired product to the total amount of toluene consumed in the process. The reaction, too, must be of such a nature as to proceed with a sufficiently high velocity to be profitable.

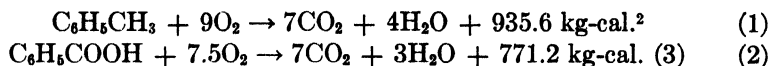
A number of non-reactive vapors or gases have been suggested for use as diluents for the air used in vapor phase oxidation. It may be that in some cases a diluent tends to blanket side reactions which take place. Other diluents merely decrease the concentration of one or more of the reactants and thereby lessen the speed of the reaction.

Water vapor added to the reacting gases may serve as a means of carrying some of the less volatile products from the reaction chamber. However, if water is a product of the desired reaction, its addition may have a detrimental effect. The addition of any vapor or gas to the reactants increases the velocity with which they pass over the catalyst surface and therefore decreases the time of contact.

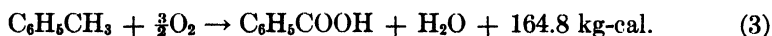
Perhaps the greatest benefit of the addition of inert materials to the reaction mixture is the tendency of these materials to maintain a more uniform temperature of the catalyst by absorbing some of the heat liberated in the reaction. If the reaction takes place at points on the surface of the catalyst, the heat liberated at these points may raise their temperature to such an extent that the products of the reaction will be different

from those which would have been obtained had the temperature been held constant. Investigators (8) using glass apparatus report that when air and toluene vapor are mixed and passed over a catalyst heated to a temperature of from 200 to 300°C., points on the surface of the catalyst are heated to redness by the heat liberated in the reaction.

The following thermal equations show that a large quantity of heat will be liberated when the desired reaction takes place.



By subtracting equation 2 from equation 1 we get the following equation:



If one molecular weight of toluene is completely oxidized, there are 935.6 kg-cal. of heat liberated. Nine molecular weights of oxygen will be consumed in the process. However, if nine molecular weights of oxygen are utilized to oxidize toluene to benzoic acid, there will be 6×164.4 kg-cal. of heat liberated. This amounts to 50.8 kg-cal. more than the amount liberated when this same weight of oxygen is consumed in the complete oxidation of toluene.

The temperature at which a particular reaction may be catalyzed is dependent upon the catalyst used. For example, if a mixture of air and toluene vapor is passed over a vanadium pentoxide catalyst, the temperature must be nearly 400°C. before an appreciable amount of benzoic acid is formed. If some other catalyst is used, this same mixture will react at a different temperature.

EXPERIMENTAL PROCEDURE

The work herein reported was done in an attempt to determine the applicability of a tin vanadate catalyst to the vapor phase oxidation of toluene to benzoic acid. The effect of preliminary heating upon the activity of tin vanadate and the effects of such variables as reaction temperature, concentration of oxygen, and the addition of diluent gases were studied. Not only was the percentage of toluene converted to benzoic acid determined, but also a measure was taken of the extent to which the toluene was completely oxidized.

The apparatus consisted of a reaction chamber of black iron 3 in. long and $1\frac{1}{2}$ in. in diameter fitted at the bottom end with a cap and at the top with a reducer, T. The lower cap was drilled and threaded to take a $\frac{1}{2}$ -in. pipe through which the gases might enter the reaction chamber. The gases passed up through the catalyst and out of the chamber through the

² This is the average of the values given by Kharasch (5).

side arm of the T. The upper opening of the T was bushed down to take a $\frac{1}{4}$ -in. pipe which extended down to the top of the catalyst. This last named pipe was capped at the lower end and carried a copper-advance thermocouple for measuring the temperature of the gases as they came from the catalyst. Since the position of maximum temperature in the

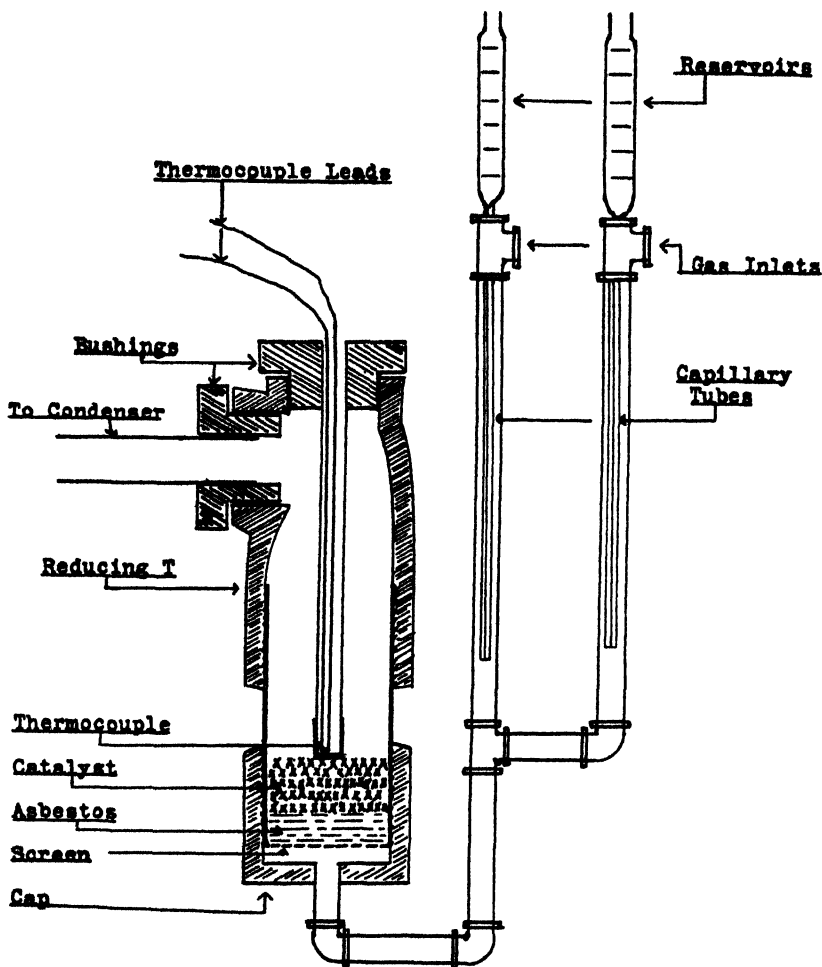


FIG. 1. Diagram of the apparatus (approximately two-thirds actual size)

body of a catalyst varies from time to time and is dependent upon the age of the catalyst, rate of gas flow, and other conditions, the temperature of the gas coming from the catalyst was taken as the working temperature of the catalyst. A diagram of the apparatus used is shown in figure 1.

The entire apparatus with the exception of the reservoirs and the con-

denser was placed in a tin can $8\frac{1}{4}$ in. tall and $6\frac{1}{2}$ in. in diameter on the inside of which 30 ft. of No. 16 B. and S. gauge chromel wire was imbedded in alundum cement. The chromel wire acted as the heating unit and was placed in series with an outside resistance. After the apparatus was placed in the can in the desired position the remainder of the can was filled with sand. This was done so that all parts of the apparatus would be held at a uniform temperature. The variation in temperature of the gases coming from the catalyst never amounted to more than 2°C . for a given run.

Toluene was placed in the reservoir by means of a calibrated pipet and forced into the furnace at the desired rate through the connecting capillary. Since the capillary tube was heated to a temperature well above the boiling point of toluene, this material was vaporized before it reached the bottom end of this tube. At this point the vapor came in contact with the incoming air. Ample mixing of the vapor with the air took place as the two materials passed through the iron tube leading to the catalyst chamber and in their passage through the asbestos catalyst support. The desired rate of toluene flow was obtained by means of mercury leveling bulbs which regulated the pressure on the surface of the toluene in the reservoirs.

The gas flow into the furnace was kept constant throughout the run and for 90 minutes after the last of the toluene had entered the furnace. This was done in order that the greater portion of the benzoic acid which had been formed would be carried from the furnace.

In all of the work to be reported here 2 cc. of toluene (1.707 g.) was fed into the furnace in thirty minutes. After the washing period was finished the benzoic acid which had been formed was washed from the condenser with alcohol and water.

Any carbon dioxide which remained in the solution washed from the condenser was removed before the benzoic acid was titrated. This was done by bubbling carbon dioxide-free air through the solution for forty minutes. The acid was then titrated with *N*/10 sodium hydroxide solution which had been standardized against c.r. benzoic acid. Phenolphthalein was used as indicator.

The first run made under a given set of conditions was discarded; data were collected from subsequent runs. The 90-min. wash period was not sufficient to remove all of the benzoic acid from the furnace, but it was considered reasonable to assume that the amount of acid which was carried over from one run to the next would be constant. Any inaccuracy due to this carry-over from one run to the next was less than the inaccuracies due to errors which might develop from other sources.

The escaping gas from the condenser was passed through concentrated sulfuric acid to remove the vapors of water and toluene. Next, it passed through two weighed tubes of potassium hydroxide solution (sp. gr. 1.27),

and finally through a weighed tube of concentrated sulfuric acid with a glass wool filter on the end. The difference in the sum of the weights of the potassium hydroxide tubes and the weighed sulfuric acid tube before and after the run was taken as the weight of the carbon dioxide produced. The removal train was connected to the condenser during the time toluene was being fed into the furnace and for five minutes after the last of the toluene had entered the furnace. The weight of carbon dioxide found in this manner was not entirely accurate, but the method served as a means of determining the relative losses of starting material.

The back pressure created by the carbon dioxide removal train was relieved by means of an aspirator. In this way it was possible to keep the pressure within the reaction chamber equal to that of the atmosphere.

The tin vanadate used as catalyst in this work was prepared by precipitation. A hot solution of carefully purified ammonium metavanadate was added to a dilute solution of stannic chloride (sp. gr. 1.075) to precipitate the tin vanadate. The product was washed several times by decantation. It was then filtered on a Büchner funnel and washed until the filtrate was practically free of chlorides.

When the washing was completed, the material was transferred to a large evaporating dish and dried for thirty-six hours at 110°C. The drying process was hastened by breaking up the lumps and by stirring the material occasionally. The dried tin vanadate was a rather hard, brittle material and was chocolate colored. It was broken up by means of a mortar and pestle until it would pass through a 20-mesh sieve.

The tin vanadate prepared as described above was divided into three parts, one of which was used directly as the contact mass in the oxidation of toluene to benzoic acid. This unheated material will be spoken of as catalyst A. Another portion of the material was placed in a cold muffle furnace and slowly heated to 400°C., maintained at that temperature for thirty minutes, and then allowed to cool. Tin vanadate treated in this manner will be spoken of as catalyst B. The third portion of the untreated material was heated in a furnace at 700°C. for thirty minutes. This material will be called catalyst C. When the temperature of the furnace in which catalyst C was being heated reached 450°C., some ammonium chloride was expelled from the material. The heated catalysts took on a yellowish color.

The apparent volume of catalyst used in each case was 30 cc. The material was spread evenly over the asbestos base, so that the reacting gases would pass through equal thicknesses of the contact mass.

Before any data were taken the catalysts were used for several days in the oxidation of toluene so that they would reach a constant degree of activity. This precaution was apparently unnecessary, as there was little or no change in the activity noticed after a few runs had been made.

RESULTS

The data in table 1 are made up of the results of a series of runs carried out in an attempt to determine the temperature at which the conversion of toluene to benzoic acid would be most practical. These data are represented graphically in figures 2 and 3. It is apparent that the temperature at which the highest percentage of toluene is converted to benzoic acid is 243°C., and that the percentage of toluene completely oxidized increases rapidly with increasing temperature.

On comparing the different catalysts, it is seen that the heating of tin vanadate changes its nature to a considerable extent. The exact nature of this change has not been determined, but it may be due to the driving off of occluded ammonium chloride. It is possible, too, that a change in

TABLE 1

Determination of most practical temperature for the conversion of toluene to benzoic acid
Air flow: 7 liters per hour, which represents 100 per cent of the amount of oxygen required to oxidize the toluene to benzoic acid. Toluene flow:
3.414 gm. per hour (2 cc. in 30 minutes)

TEMPERATURE IN °C	PER CENT TOLUENE CONVERTED TO BENZOIC ACID USING CATALYSTS			PER CENT TOLUENE CONVERTED TO CARBON DIOXIDE USING CATALYSTS		
	A	B	C	A	B	C
210	8 50	6 45	3 83	5 51	5 95	2 64
221	9 72	8 59	5 25	11 02	11 42	3 73
228	10 55	9 55	7 90	14 10	13 79	8 45
243	11 00	9 75	11 90	19 80	17 93	20 62
246	9 80	9 29	9 80	22 82		
261	7 17	7 85	7 17	25 42	19 48	21 60
270	6 45	7 61	6 45	27 43	22 70	21 70

crystalline structure took place during the heating period. Appreciable sintering of tin vanadate takes place at a little higher temperature than that to which catalyst C was heated.

In order to ascertain the effect of oxygen concentration upon the amount of toluene converted to benzoic acid and upon the amount of toluene completely oxidized, a series of runs were made using different rates of air flow. The temperature chosen for these runs was 236°C. At this temperature the conversion of toluene to benzoic acid was of the same order for all three catalysts, and there was no danger of exceeding the optimum operating temperature of any of them. The results of this series of runs are shown in table 2.

The data in table 2 indicate the effect of variation of oxygen concentration upon the percentage of toluene changed to benzoic acid and upon the percentage of toluene completely oxidized. The data show clearly that

even though the percentage of toluene converted into benzoic acid is somewhat higher at the higher oxygen concentrations, the loss of toluene as carbon dioxide and water is very much greater at these concentrations. In the production of benzaldehyde from toluene by the use of air as the oxidizing agent in the presence of a vanadium pentoxide catalyst, Green (4) states that equimolecular quantities of oxygen and toluene vapor give good results and that Gibbs has indicated that two and one-half times

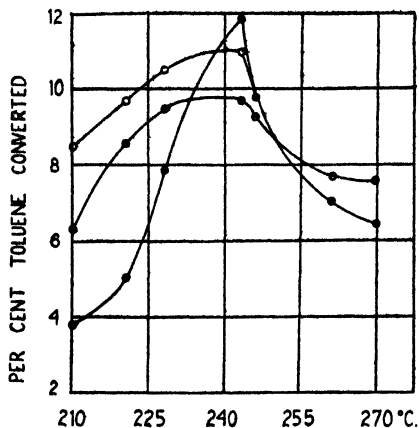


FIG. 2. The effect of temperature upon the per cent of toluene converted to benzoic acid. O, catalyst A; \ominus , catalyst B; \oplus , catalyst C.

TABLE 2

The effect of oxygen concentration

Temperature: 236°C. Toluene flow: 3.414 g. per hour (2 cc. in 30 minutes)

AIR USED IN PER CENT OF THEORY	PER CENT OF TOLUENE CONVERTED TO BENZOIC ACID USING CATALYSTS			PER CENT OF TOLUENE CONVERTED TO CARBON DIOXIDE USING CATALYSTS		
	A	B	C	A	B	C
50	8 57	8 04	6 05	11 05	9 95	4 18
71.5	8 66	8 43	6 13	11 31	11 32	4 54
100	9.29	9 47	9 47	19 37	16 05	11.91
143	9 15	10.12	11.10	20 95	20 59	18.92

that concentration is desirable. The data in table 2 show plainly that even lower oxygen concentrations are desirable in the production of benzoic acid from toluene by the use of a tin vanadate catalyst. The great change in the amount of carbon dioxide produced with changing oxygen concentrations makes it apparent that a delicate means of control for the air flow is essential in this type of work. A graphical representation of the effect of oxygen concentration upon the percentage of toluene converted to benzoic acid is given in figure 4.

A relative measure of the amount of toluene consumed per pass which was converted to benzoic acid is given in the data in tables 3 and 4. The data in these tables were compiled by adding the per cent of toluene converted to benzoic acid to the per cent lost by complete oxidation. The per cent converted to benzoic acid was divided by this sum; the quotient obtained in this manner was then multiplied by 100. This final value shall be called the conversion ratio.

The data in table 3 show the effect of temperature upon the conversion ratio. Since there may have been some error in the carbon dioxide determination the values given are only relative. These data show that the

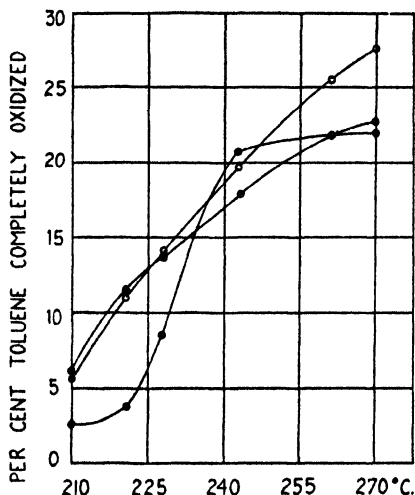


FIG. 3

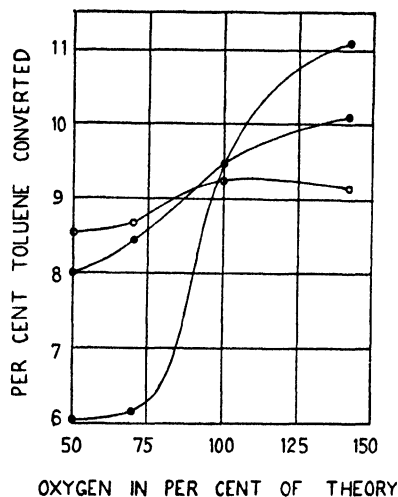


FIG. 4

FIG. 3. The effect of temperature upon the per cent of toluene completely oxidized. O, catalyst A; ⊖, catalyst B; ⊕, catalyst C.

FIG. 4. The effect of oxygen concentration upon the per cent of toluene converted to benzoic acid. O, catalyst A; ⊖, catalyst B; ⊕, catalyst C.

conversion ratios for all three catalysts decrease with increasing temperature. Although the ratio for catalyst B is lower than the ratios of the other two catalysts at the lower temperatures, it is higher than the other ratios at the higher temperatures. The values of the different ratios were almost the same at the temperature at which the greatest percentage of toluene was converted to benzoic acid per pass (243°C.).

The data in table 4 show the effect of oxygen concentration upon the conversion ratios of the different catalysts studied. It is shown by these data that the higher the oxygen concentration the higher the losses of toluene by complete oxidation. At the temperature chosen the conversion ratio for catalyst C is consistently higher than the ratios of the other two catalysts.

The variations of conversion ratios from one catalyst to another indicate that there is an essential change brought about in the catalytic activity of tin vanadate by preliminary heating. These differences suggest the possibility of finding a catalyst which under the proper conditions would convert a greater portion of the toluene consumed to benzoic acid. Had this ratio been the same for all of the catalysts under the same set of conditions, the prospects for finding a better catalyst would have been small. It may be possible to find some foreign substance which when added to tin

TABLE 3

The effect of temperature upon the conversion ratio

Air flow: 7 liters per hour (100 per cent of the amount necessary to oxidize all of the toluene to benzoic acid). Toluene flow: 3.414 g. per hour (2 cc. in 30 minutes)

TEMPERATURE IN °C.	PER CENT OF TOLUENE CONSUMED WHICH WAS CONVERTED TO BENZOIC ACID USING CATALYSTS		
	A	B	C
210	60.7	52.1	59.1
221	46.9	42.9	58.4
228	42.8	40.8	48.2
243	35.7	35.2	36.6
261	22.4	28.7	25.0
270	18.7	25.2	23.8

TABLE 4

The effect of oxygen concentration upon the conversion ratios of the catalysts

Temperature: 236°C. Toluene flow: 3.414 g. per hour (2 cc. in 30 minutes)

AIR USED IN PER CENT OF THEORY	PER CENT OF TOLUENE CONSUMED WHICH WAS CONVERTED INTO BENZOIC ACID USING CATALYSTS		
	A	B	C
50.0	44.5	44.7	59.0
71.5	43.5	42.6	57.5
100.0	32.4	37.1	44.3
143	30.4	33.1	37.0

vanadate will blanket the reaction in which carbon dioxide is formed and thus produce a higher conversion ratio. This assumption is substantiated by the work of Charlot (1) in which he used various catalysts in the oxidation of toluene and its derivatives and found that there was a close relation between the extent of complete oxidation and the catalyst used. This relation was different for different catalysts, but it was essentially the same for a given catalyst irrespective of the compound oxidized.

In order to determine whether or not the addition of carbon dioxide to

the reacting gases would produce a higher percentage of benzoic acid from toluene, a series of runs was made in which carbon dioxide was added to the mixture of air and toluene vapor. The results of this series of runs are shown in table 5.

The data in table 5 indicate that the addition of carbon dioxide to the reacting gases has no beneficial effect,—at least there is no increase in the amount of benzoic acid produced per pass. Since no measure was taken of the extent of complete oxidation, we are not in a position to say definitely how the presence of carbon dioxide affected the conversion ratio, but in view of the other work which has been done on this subject, it is likely that the conversion ratio was not affected to any great extent. The decrease in the benzoic acid yield was probably due to the increased velocity of gas over the catalyst. A run was made with an air velocity of 3.5 l. per hour and with the same velocity of carbon dioxide. The oxygen concentration in this case was 50 per cent of the theoretical amount required to oxidize the toluene to benzoic acid, while the total gas velocity

TABLE 5

Runs made in which carbon dioxide was added to the mixture of air and toluene vapor
Catalyst: tin vanadate heated to 400°C. Temperature, 236°C. Air flow: 7 l. per hour (100 per cent theoretical oxygen)

CARBON DIOXIDE ADDED IN LITERS PER HOUR	PER CENT TOLUENE CONVERTED TO BENZOIC ACID
None	10.67
5	8.91
10	7.26

was essentially the same as when the oxygen concentration was 100 per cent and no carbon dioxide was added. The benzoic acid produced under these conditions was the same as when none of the diluent was added.

When water vapor was added to the reacting gases, the extent of complete oxidation was the same as when no water vapor was added, and the benzoic acid yield was appreciably decreased.

In all of the work herein reported small quantities of anthraquinone and benzaldehyde were formed. Although no measure was taken of these quantities, the anthraquinone production appeared to increase with increasing temperature and also with the addition of carbon dioxide to the reaction mixture.

CONCLUSIONS

1. Tin vanadate is an excellent catalyst for the oxidation of toluene to benzoic acid.

2. Heating previous to use has a marked effect upon the behavior of tin vanadate as a catalyst in the reaction studied.

3. The temperature at which the reaction takes place and the concentration of oxygen affect the ratio of carbon dioxide to benzoic acid produced in the reaction.

4. The addition of diluents to the reacting gases gave no beneficial results in any of the experiments carried out.

5. Delicate control of air flow and temperature are essential in the type of work herein reported.

6. Anthraquinone and benzaldehyde are by-products of the reaction.

REFERENCES

- (1) CHARLOT: *Bull. soc. chim.* **53**, 572 (1933); *Chem. Abstracts* **27**, 5726 (1933).
- (2) COQUILLION: *Compt. rend.* **80**, 1089 (1875).
- (3) DICKENSON: *Bur. Standards Bull.* **11**, 189 (1915).
- (4) GREEN: *Industrial Catalysis*. The Macmillan Co., New York (1928).
- (5) KHARASCH: *Bur. Standards J. Research* **2**, 359 (1929).
- (6) MAXTED: *J. Soc. Chem. Ind.* **47**, 101 (1928).
- (7) WEISS AND DOWNS: *J. Ind. Eng. Chem.* **12**, 228 (1920).
- (8) WOOG, PAUL: *Compt. rend.* **145**, 124-6 (1907).

AN EXPERIMENTAL TEST OF THE IDENTITY OF ELECTROKINETIC POTENTIALS

ELECTROSMOSIS AND STREAMING POTENTIAL MEASUREMENTS WITH A GLASS SLIT

ROBERT DUBOIS AND ALEXANDER HUNTER ROBERTS¹

Department of Chemistry, Stanford University, California

Received April 11, 1935

Because of the extensive use and the great importance of electrokinetic methods in the study of adsorption from solution, the stability of colloidal systems, the electrical charges on colloids, living cells, etc., and a variety of other properties dependent on the existence of an electrical double layer at an interface, it is of importance to know whether the results of different electrokinetic experiments can be compared with each other, or, more specifically, whether the electrokinetic, or zeta, potentials obtained by one type of electrokinetic measurement are identical with those obtained by another method.

It has generally been assumed that cataphoresis, electrosmosis, or streaming potential experiments would yield identical values of the ζ -potential provided the system being studied were in exactly the same condition in each case. This assumption is partly due to a rather prevalent notion that the classical mathematical formulations of electrokinetics require such an identity and partly to Saxén's (23) experimental demonstration of the so-called reciprocal relation between electrosmosis and streaming potential

$$\left(\frac{V}{I} = \frac{E}{P}\right)$$

which he showed must obtain if the identity assumption is made with regard to the ζ -potentials.

Since the Saxén experiments of 1892 very little has been done to supply additional evidence on this important point. Thon (24) called attention to the fact that electrokinetic potentials calculated from cataphoresis measurements passed through maxima or minima at electrolyte concentrations considerably different from those at which maxima or minima occurred in streaming potential or electrosmosis experiments. Kanamaru

¹ Present address: Department of Chemistry, Fresno State College, Fresno, California.

(12) has made extensive electrosmosis and streaming potential measurements on cellulose and cellulose derivatives in contact with water and numerous electrolyte solutions, and reports that the streaming ζ -potentials were 2.6 times as large as the electrosmosis values. Since our own experiments were completed Bull (5) has reported a careful investigation of the same question. Electrosmosis, streaming potential, and electrophoretic measurements were made with Pyrex glass coated with protein. The ζ -potentials were found to be identical in the three cases.

Briggs (4) measured streaming potentials produced by streaming buffer solutions through diaphragms made of quartz particles covered with egg albumin. The ζ -potentials calculated from his data are in remarkably close agreement with those reported by Abramson (1, 10) on the basis of measurements of cataphoresis of quartz particles coated with egg albumin. However, the buffer solutions used in the two sets of experiments differed in electrolyte content, and Abramson (2) repeated the cataphoresis measurements with protein-covered quartz particles and buffers identical in composition with those used by Briggs. The ζ -potentials were now found to be about 50 per cent higher than Briggs' values, and Abramson concluded that the proteins used must have differed in some way.

In addition to these direct comparisons of electrokinetic potentials, it may be mentioned that deviations from the Helmholtz equations have been reported and discussed by various workers, including Gösta Köhler (13), Manegold and Solf (16), H. Reichardt (20, 21, 22), and Ettisch and Zwanzig (7). H. B. Bull has recently repeated the measurements of Ettisch and Zwanzig (6) and finds the deviations not to exist.

In order to provide a further, independent test of the identity of electrokinetic potentials we undertook to make combined measurements of electrosmosis and of streaming potential on a single system. We chose for the experiments a glass slit made of optically polished glass and of known dimensions. This was generously put at our disposal by Professor J. W. McBain and was the largest (slit No. 10) of the glass slits used in his careful measurements of surface conductivity (15). A detailed description of the preparation of these slits is given in the paper referred to. The dimensions of the slit were checked by us and found to agree with those published; namely, thickness (t), 0.00125 cm.; width (w), 1.001 cm.; length (l), that is, the thickness of the supporting block containing the slit, 0.5014 cm.; cross section of slit (wt), 0.00125 cm.²

APPARATUS

The Pyrex glass apparatus in which the slit was mounted is shown in figure 1, the letters of which refer to the following parts: S, glass block containing the slit; BB, glass end blocks about 2.5 cm. square, with an opening through them about 1.3 cm. square; F, ebonite clamps holding

together slit block, end blocks, and main cell; CC, capillary tubes about 30 cm. long, graduated in millimeter scale divisions and calibrated at 1-cm. intervals along their length by a weighed mercury thread,—used for observing displacement of liquid through slit; E, saturated calomel electrodes, separated from the rest of the apparatus by porous plugs, PP, of sintered glass; E_p , probing electrodes of bright platinum; R, connections of rubber tubing; D, screw clamps.

This apparatus (denoted cell IV) was designed to replace an earlier form equipped with platinized platinum probing electrodes and glass stopcocks throughout. The difficulties experienced with the earlier apparatus (denoted cell III) were (a) contamination of the very dilute solutions by

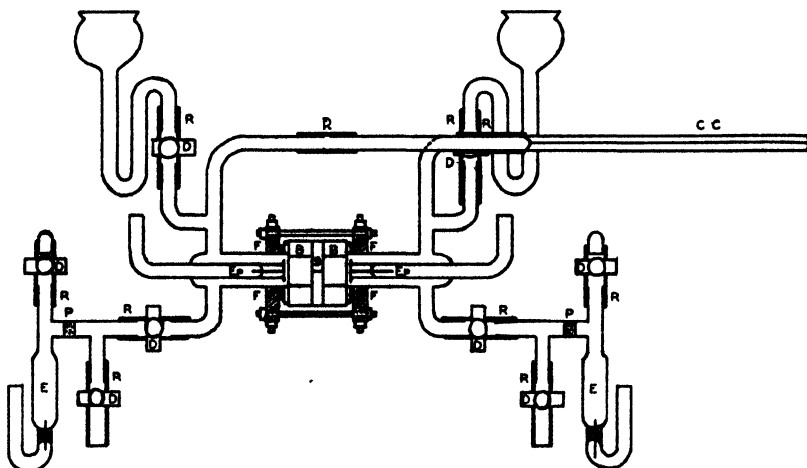


FIG. 1. Apparatus for electromosmosis and streaming potential measurements with glass slit. S, block containing slit; C,C, capillary tubes; E,E, calomel electrodes; E_p and E_p , platinum probing electrodes; F,F, ebonite clamps; B,B, glass end block; R, rubber tubing; D, screw clamp; P, P, porous plug of sintered glass.

foreign electrolyte previously adsorbed on the porous platinum surfaces of the probing electrodes, (b) persistent leakage through the glass stopcocks, and (c) contamination by stopcock grease. The new apparatus was entirely free from these sources of error. To test the rate of contamination from the rubber tubing and other sources in cell IV the solution used in experiments 21 and 22 was allowed to remain in the cell ninety-one hours and experiment 23 was conducted. The results showed that the rate of contamination was no greater than would be expected for conductivity water in any type of container. The rate of increase of the specific conductance of the conductivity water in the special Jena glass storage flasks was about 1 per cent per day.

At intervals the cell was cleaned with chromic acid without disassem-

bling, and then rinsed with conductivity water for a period of about three days before resuming measurements, the water being forced through the slit by pressure. The cell was cleaned as described between the successive experiments 26-27, 43-54, and 61-87. Dilute nitric acid was used for cleaning between experiments 113 and 114. Mercury for the electrode arms was cleaned by distillation in the absence of air.

PREPARATION OF SOLUTIONS

The conductivity water used in these experiments was prepared in a special still (3) and was stored in Jena glass flasks properly protected against atmospheric contamination. The specific conductance was always determined immediately before use. The electrolyte solutions were made up to weight normality from samples of the salts, which were the purest obtainable on the market and were used without further purification. The glassware used was always steamed thoroughly and rinsed with conductivity water. The specific conductances of the more dilute electrolyte solutions were measured directly; the others were obtained from the International Critical Tables and the Landolt-Börnstein-Roth *Physikalisch-Chemische Tabellen*, were recalculated to 22°C., and were corrected for the conductivity of the solvent. The values are given in the later tables.

METHOD OF MEASUREMENT OF ELECTROSMOSIS

The quantities directly measured in the electrosmosis experiments and the methods of obtaining them are indicated in what follows.

V , the electrosmotic flow (cc. per second), was calculated from the average of the displacements of the liquid menisci in the two capillary tubes and the duration of the experiment.

E_r , the total E.M.F. applied at the calomel end electrodes, was obtained from 45 volt "B" batteries in series, which served excellently as sources of steady voltage because of the very slight current drain.

E_0 , the potential drop across the probing electrodes. To measure this a compensating E.M.F. exactly equal and opposite to E_0 was applied to the probing electrodes by means of a potentiometer supplied by "B" batteries and shunted at the output terminals by a calibrated Weston voltmeter. Between one of the output terminals and its connection to the probing electrode was inserted a sensitive galvanometer. When the E.M.F.'s were balanced, as shown by the absence of any current through this galvanometer, the value of the compensating E.M.F. was read directly from the voltmeter. This method did not disturb the electrosmosis experiment in progress but, on the contrary, had a steadying effect on the working current, which had often varied considerably when a quadrant electrometer had been used to measure E_0 . The values of E_0 appearing in the tables are the means of three such determinations made during each experiment.

I_0 , the current passing through the slit during electrosmosis, was measured by means of a sensitive galvanometer connected in series with the slit and calibrated at frequent intervals. In experiments with highly conducting electrolyte solutions a 0 to 999.9 ohms four-dial resistance box was used as a shunt around the galvanometer to bypass part of the current.

E_{sl} , the effective E.M.F. across the ends of the slit, was obtained by multiplying the current I_0 by the resistance of the liquid in the slit, R_{sl} (see below). It is important to note that the magnitude of the electrosmotic effect depends on the value of the electrical field *within the slit*, that is, on E_{sl}/L , and the potential difference E_{sl} is somewhat less than E_0 because of the potential drops between the probing electrodes and the ends of the slit. In order to evaluate these IR drops an extended study was made of the series resistances in the circuit. As a result it was possible to evaluate separately the resistance R_{sl} and thus the potential difference E_{sl} ($= I_0 \times R_{sl}$).

ζ -potentials were calculated from the experimental data by use of equation 1, which was derived by Helmholtz for a capillary tube and can be shown to be applicable without change to a narrow slit:

$$\zeta = \frac{4\pi\eta}{D} \cdot \frac{L}{Q} \cdot \frac{V}{E} \quad (\text{all quantities in absolute units}) \quad (1)$$

where η is the viscosity of the liquid within which the double layer lies (taken equal to the viscosity of the bulk liquid), D is the dielectric constant of the liquid in the same region (taken equal to 80 here), L is the length of capillary or slit, Q its cross section, E the potential difference at its ends (equal to E_{sl} here), and V the electrosmotic flow (cc. per second).

With substitution of the numerical values and change to practical units,

$$\zeta \text{ (in millivolts)} = \frac{4 \times 3.1416 \times 0.01}{80} \times \frac{0.5014}{0.001251} \times (300)^2 \times \frac{V}{E_{sl}}$$

METHOD OF MEASUREMENT OF STREAMING POTENTIAL

The data obtained from the streaming potential experiments and the methods used were the following:

V , the rate of flow of the liquid through the slit during the streaming, was obtained from the observed displacement of liquid in the capillary tube left open during the experiment.

P , the applied hydrostatic pressure, was obtained by the use of mercury in a reservoir whose height could be adjusted and which was separated from the reservoir containing the streaming solution by a glass tube to which was connected a mercury manometer. The readings of the manometer were corrected for the difference in water levels in the reservoir and the outlet of the cell.

E_s , the streaming potential. In the early experiments with cell III streaming potentials were measured directly by the deflections of a Compton electrometer connected to the calomel electrodes (one connection through ground). This was a sensitive quadrant electrometer (1000 mm. deflection per volt with scale at one meter), and although the instrument and all connections to it were carefully shielded, considerable difficulty was caused by the unsteadiness of the zero point arising from the large deflections obtained. In the later experiments with cell IV this difficulty was avoided by the use of an improved method of measurement. Figure 2 shows the circuit arrangement. The streaming potentials were measured with a Leeds and Northrup Type K potentiometer with the Compton electrometer as a null instrument. By this method the electrometer vane was subjected to only slight displacements while a setting was being

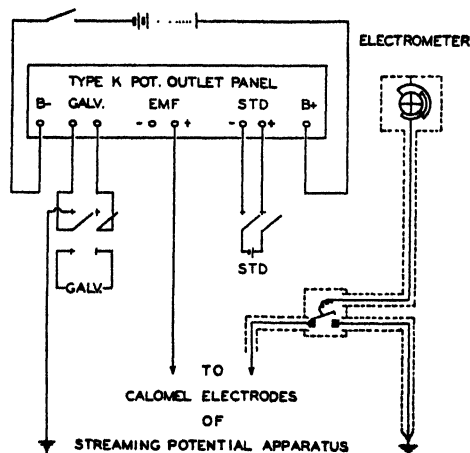


FIG. 2. Electrical circuit for measurement of streaming potential

obtained, so that the zero point was very stable. It was necessary to operate the potentiometer at the high range (0 to 16.1 volts) to accommodate the large streaming potentials often obtained. A group of 6-volt storage batteries supplied the working current for the potentiometer. These were always recharged slowly and gave a constant voltage over long periods of time.

Calomel electrodes saturated with potassium chloride were used for all streaming potential measurements. The maximum error in the measurements of E_s was not more than 0.1 per cent, except in the few experiments where E_s was only a few millivolts.

The potentiometer, cell, and reservoir were placed on plate glass resting on grounded sheet iron.

κ_s , the apparent specific conductance of the liquid in the slit, was calcu-

lated from the known dimensions of the slit and the observed conductance of the liquid in the slit. This slit conductance ($1/R_{sl}$) was determined before and after each set of streaming potential measurements. For this purpose the slit was flushed out with fresh solution, a known E.M.F. of, say, 90 volts, was applied to the calomel end electrodes (disconnected, of course, from the electrometer), and I_0 , E_0 , E_{sl} , and R_{sl} were determined as in the electrosmosis experiments.

TABLE 1
Electrosmosis experiments with conductivity water

NO.	TEMP °C	κ MHOS/ CM. $\times 10^6$	E_T VOLTS	E_0 VOLTS	E_{sl} VOLTS	V CC PER SEC $\times 10^3$	I_0 AM- PERES $\times 10^7$	V/I_0 CC AMP SEC. $\div 3 \times 10^9$ $\times 10^6$	$\frac{u_{EO}}{CM.^2}$ VOLT-SEC $\times 10^5$	ζ MILLIVOLTS
19	23	0 53	135	105.0	104 2	-17 2	6.75	8 22	67 7	-95 8 \pm 2 5
20	24	0 53	22 5	16 7	16.1	-2.0	0 96	7.14	50 9	-72 0 \pm 4 7
21	23	0 53	45	30 4	29 4	-4 6	1 70	9.04	61 6	-84 7 \pm 5 5
22	23	0 53	90	56.7	54.6	-8 8	3 48	8 20	63 1	-89 3 \pm 7 5
24	22	0 73	135	106 8	104 2	-14 8	5 54	8 97	57 2	-81 0 \pm 4 8
25	22	0 73	135	104 2	101 7	-14 1	5 39	8 71	55 7	-78 8 \pm 5 0
26	22	0 73	90	71 6	69 9	-8 8	3 62	8 21	50 7	-71 7 \pm 4 7
27	22	0 56	225	122 3	116.0	-23 6	10.70	7 42	81 0	-114 6 \pm 7 3
28	22	0 56	180	115 5	87 8	-16 0	8 09	6 74	72 3	-102 2 \pm 7 7
29	24	0 56	135	72.0	68 3	-12 6	6 46	6 54	73 4	-103 9 \pm 11 9
30	24	0 56	90	49.1	46.6	-8 2	4.43	6 20	71 0	-100 4 \pm 11 4
31	25	0 56	45	25 4	24.1	-4 1	2 35	5 90	70 4	-99 5 \pm 19 0
Mean.....								7 65	64 0	-91 6 \pm 7 2

The ratio V/I_0 is in absolute units—cc. per second per ampere/ 3×10^9 —in order to facilitate comparison with the streaming potential ratio E/P , also in absolute units

ζ -potentials were calculated from the experimental data by the use of equation 2, valid for slit or capillary:

$$\zeta = \frac{4\pi\eta}{D} \cdot \kappa_s \cdot \frac{E_s}{P} \quad (\text{all in absolute units}) \quad (2)$$

or, in practical units,

$$\zeta = \frac{4 \times 3.1416 \times 0.01}{80} \times \kappa_s \times 9 \times 10^{11} \times \frac{E_s}{P} \times 10^3$$

(ζ in millivolts, E_s in volts, and P in dynes per square centimeter).

ELECTROSMOSIS EXPERIMENTS WITH CONDUCTIVITY WATER

Three series of electrosmosis experiments were carried out with three different lots of conductivity water of nearly the same conductivity

(0.5 to 0.7×10^{-6} mho per centimeter), fifty-seven separate determinations of ζ in all.² The results are given in table 1.

Before making a set of measurements the apparatus and the slit were rinsed thoroughly (while assembled) with conductivity water whose specific conductance had just previously been determined. The positions of the water menisci in the capillary tubes were then read after previous observations had shown them to be stationary without applied field. The desired voltage was then applied to the calomel end electrodes and the time noted to the nearest second. From two to four times during the ensuing electrophoresis the total current passing through the slit was read from the series galvanometer and the potential difference between the probing electrodes (E_0) was measured without interruption of the experiment. At the end of from three to ten minutes the current was interrupted; the water menisci in the capillaries instantly became stationary, and their positions were read.

Each set of data in the tables is the mean of the results of from four to six such experiments carried out in succession at the same applied voltage and without refilling the apparatus. The last column in table 1 gives the mean deviation of the individual ζ -potentials from the recorded mean.

The direction of electrophoresis was generally reversed in successive experiments by reversing the applied field. The mean of the ζ -potentials thus obtained was 11.7 per cent less for experiments in one direction (thirty experiments) than for those in the reverse direction (twenty-seven experiments), or 4.2 per cent less than the published mean for all experiments.

The work with conductivity water was entirely completed before that with electrolyte solutions was begun, in order to avoid as far as possible contamination of the slit by foreign electrolyte.

Relation of observed electrophoresis to strength of applied field

We were much interested in the possibility of finding a dependence of the ζ -potential on the applied field, which would show up in a variation of the quantity V/E . Toward this end the experiments were carried out over a tenfold range in the applied voltage. In figure 3 we have plotted the observed values of the ratio V/E_{sl} against the effective voltage E_{sl} , also the average values of the ratio V/E_T , for all experiments at the same total voltage, against E_T . The plot shows only a random variation in V/E_{sl} and only a very slight variation in V/E_T . It is evident that in the range of these experiments the charge distribution in the electrical double layer at the glass-water interface has been unaffected by the increase in the strength of the external electrical field applied parallel to the interface. It would perhaps be more accurate to say that the highest field strengths used

² These do not include twenty earlier and much less reliable measurements made with the same slit mounted in a different apparatus (cell III, see p. 3).

were insufficient to effect a displacement of parts of the double layer which were sessile under the influence of the lowest fields. We are inclined to predict, however, that with sufficiently large applied electromotive force such a displacement, or slipping, might be brought about, with a consequent increase in the apparent value of the electrokinetic potential, ζ .

Absence of time effect in electrosmosis

In his early experiments on electrosmosis through a glass capillary tube Quincke (19) noticed that the electrosmotic flow was much more rapid just after the apparatus had been filled than after it had stood twenty-four hours. He attributed this fact to slow solution of the glass, which he actually demonstrated to have taken place. A parallel increase in the

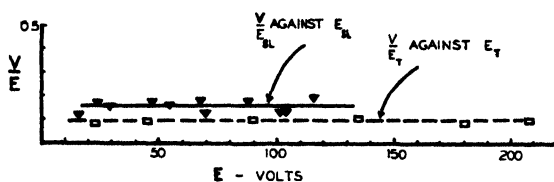


FIG. 3. Relation of electrosmotic flow, V , to applied field, E

TABLE 2

Absence of time effect in electrosmosis experiments

NO	E_T VOLTS	E_0 VOLTS	E_{sl} VOLTS	E_0/E_T	E_{sl}/E_0	V CC/SEC $\times 10^5$	V/E_{sl} CC/VOLT- SEC $\times 10^5$	ζ MILLIVOLTS
22	90	56.7	54.6	0.62	0.96	-8.8	0.16	-89.3
23	90	84.5	81.4	0.93	0.96	-9.6	0.12	-66.9
Hourly change							0.0004	0.25

electrical conductivity of the water was found. In our own work each series of experiments with the same filling of conductivity water occupied an interval of several hours. In order to test for a similar source of error in our own work the following experiment was carried out. At the conclusion of experiment No. 22 the apparatus was allowed to stand without rinsing or refilling. At the end of ninety-one hours experiment No. 23 was performed, using water already in the apparatus and the same applied voltage. The results in table 2 show an almost negligible hourly change. The increase in the ratio E_0/E_T indicates the effect of passage of potassium chloride from the end electrodes into the tubes leading to the main cell; the constancy in the ratio E_{sl}/E_0 shows that the electrolyte did not reach the slit.

Since examination of the results of the electrosmosis experiments fails to

show any regular dependence on applied voltage or conductivity of the water used, we shall take as the most probable values of the ζ -potential and related quantities the mean values of all of the fifty-six experiments of the three series (exclusive of No. 23). These are given in table 1. The final value of the ζ -potential for the glass-water interface thus calculated is -92 millivolts.

STREAMING POTENTIAL EXPERIMENTS WITH CONDUCTIVITY WATER

At the close of the electrosmosis experiments just described the cell and slit were cleaned and rinsed thoroughly. An extended series of streaming potential measurements was then made at different pressures with various lots of conductivity water of about the same specific conductance (0.5 to 0.7×10^{-6} mho per centimeter); one hundred thirty-five separate measurements were made in all.

TABLE 3

Comparison of the results obtained with the early cell and the improved cell

CELL	ELECTROSMOSIS		STREAMING POTENTIAL		$\frac{\zeta_{SP}}{\zeta_{EO}}$
	Number of experiments	Mean ζ	Number of experiments	Mean ζ	
		<i>mv</i>		<i>mv.</i>	
Cell IV.....	53	-92	135	-162	1.8
Cell III.....	20	-68	20	-134	2.0
Both cells.....	73	-85	155	-158	1.9

This number does not include two experiments which were evidently unreliable, and twenty earlier measurements with the slit mounted in cell III. Table 3 affords a comparison of the results obtained with the early cell (No. III) and the improved cell (No. IV).

At the beginning of each set of measurements at a given pressure a preliminary measurement was made of the rate of flow over a period of about two minutes. Before streaming was started again a reading was made of the zero point of the electrometer connected to one of the calomel end electrodes and to ground (the other calomel electrode being grounded). This reading was repeated at the close of the measurements in order to check the absence of any potential differences due to difference in the condition of the electrodes. The reading was always found to be within three millivolts of the initial value. Streaming was then started at the given pressure (always in the same direction in all experiments), and measurements of the streaming potential were made at intervals of a few minutes.

Time effect in streaming potential experiments

The streaming potentials were found to vary erratically during the first few minutes of streaming, but we found on continuing the measurements over an extended period of time that constancy was obtained after about ten minutes. In computing the published mean values of our results we have therefore excluded all observations made during the first ten minutes of streaming.³ The collected results are given in table 4, each value given

TABLE 4
Streaming potential experiments with conductivity water

NO.	TEMP °C.	κ_v^* MHOS/ CM $\times 10^8$	κ_s^* MHOS/ CM. $\times 10^8$	P DYNES CM ² $\times 10^{-4}$	V CC/SEC $\times 10^4$	V/P CM ³ DYNE-SEC $\times 10^8$	E_s VOLTS	E/P ESU DYNES/CM ² $\times 10^8$	ζ MILLI- VOLTS
34	23	0.53	6.57	2.74	0.515	1.88	0.4688	5.70	-158
35	23	0.53	6.57	5.60	1.047	1.87	0.9026	5.37	-150
36	22	0.48	6.12	2.78	0.466	1.68	0.4449	5.34	-139
37	23	0.48	6.52	5.62	0.977	1.74	0.9702	5.82	-161
39	23	0.66	6.97	51.7	9.30	1.80	7.563	4.87	-145
40	22	0.60	6.35	2.73	0.474	1.74	0.4741	5.79	-156
41	24	0.60	6.17	5.66	1.210	2.14	1.1165	6.57	-172
42	22	0.54	6.87	5.81	1.15	1.98	1.1989	6.87	-200
43	22	0.54	6.03	2.78	0.556	1.99	0.5686	6.80	-174
54	23	0.56	5.48	48.8	12.56	2.57	12.4887	8.60	-204
55	23	0.56	5.48	23.4	5.32	2.27	4.5713	6.34	-151
56	23	0.56	5.48	7.90	1.92	2.43	1.480	6.25	-148
57	24	0.56	5.48	3.21	0.709	2.21	0.5771	5.99	-143
61.1	21	0.58	2.60	48.90	11.71	2.39	16.044	10.95	-120
61.2	21	0.58	2.60	22.10	5.32	2.41	6.805	10.60	-113
61.3	21	0.58	2.60	7.94	1.93	2.43	2.138	8.96	-99
61.4	21	0.58	2.60	3.26	0.711	2.18	0.8318	8.48	-94
Mean.						2.08		6.81	-162

* κ_v and κ_s are respectively the bulk conductivity of the water used, as measured outside of the slit, and the apparent conductivity of the same water in the slit, the increase being due to the surface conductivity.

therein being the mean of from six to ten observations made during the next ten to twenty minutes.⁴

³ Similar unexplained variations in the streaming potential have been observed by other experimenters. For example, Grumbach (11) was led to adopt a rule of selection similar to ours: "Je fus amené ainsi à m'imposer comme règle de n'admettre comme valable que les forces électromotrices qui demeurent fixes à pression constante pendant au moins 10 minutes."

⁴ As a matter of fact the average value of ζ thus calculated from all measurements made after the first ten minutes of streaming (namely, -162.2 millivolts) is identical with the average obtained from *all* measurements both before and after this ten minute mark (-162.0 millivolts).

Careful plotting of the observed values of the E/P ratio against the applied pressure shows only random variation with this factor. We have therefore taken the mean of all determinations as representing the most probable value of the ζ -potential for the glass-water interface derived from streaming potential experiments. This value is -162 millivolts.

Streaming rate and applied pressure

The fundamental equations of electrosmosis and streaming potential are derived on the assumption that the flow of liquid through the slit, capillary, or porous diaphragm is non-turbulent. The usual experimental evidence of non-turbulence in streaming potential work is a constant proportionality between the rate of streaming (or the streaming potential) and the applied pressure. The data obtained from our own experiments (table 3, column 7) show that while the V/P ratio is satisfactorily constant in certain sets of measurements, it is not at all constant through the entire series of experiments. Now the rate of flow to be expected at any pressure can be calculated by use of the following equation derived for laminar flow through a slit in exactly the same way as is the Poiseuille equation for a circular tube:

$$V = \frac{wt^3P}{12\eta l}$$

where w , t , and l are respectively the width, thickness, and length of the slit, η is the viscosity of the liquid, P the difference in pressure at the ends of the slit, and V the flow rate in cc. per second. The value of the theoretical ratio V/P in the case of our slit is 3.28×10^{-8} cc. per second per dyne per cm.² The observed ratio in most of our experiments is less than this; the average value is 2.46×10^{-8} in the experiments with electrolytes and 2.00×10^{-8} with water.

This discrepancy is in the direction to be expected if the flow was turbulent. Davies and White (6a) have established that the flow of liquid through a narrow slit becomes turbulent only after the mean velocity exceeds the limit $u = 890 \eta/\rho t$, where η is the viscosity of the liquid, ρ is its density, and t is the thickness of the slit. The flow rates in all our streaming experiments were far below the critical value, and we are therefore of the opinion that turbulence did not occur in the flow of water through the slit.

The discrepancy noted forces us to suspect that the actual cross section of the slit, Q , was effectively smaller than that which we had calculated from the observed dimensions. Whether this was due to foreign intrusion in the slit, which resisted the repeated and thorough cleaning operations to which it had been subjected, or to an error in measuring the width of the slit (an error of about 0.0005 cm. would account for the discrepancy), we are unable to say. It is important, however, to point out (1) that all the ζ -potential values given here will be multiplied by a factor of $3.28/2.00$ or

TABLE 5
Electrosmosis and streaming potential experiments with water and electrolyte solutions

LIQUID	ELECTROSMOSIS				STREAMING POTENTIAL				RATIOS			
	No of expts.	$\frac{\kappa_e}{\text{cm}} \times 10^6$	$\frac{\kappa_e}{\text{cm}} \times 10^6$	$\frac{V}{I} \frac{\text{cc./sec}}{\text{e.s.u.}} \times 10^{10}$	ζ mv	No of expts	$\frac{\kappa_e}{\text{cm}} \times 10^6$	$\frac{E}{P} \frac{\text{e.s.u.}}{\text{dynes/cm}^2} \times 10^6$	ζ mv.	$\frac{\zeta_{SP}}{\zeta_{EO}}$	$\frac{E/P}{V/I}$	$\frac{\kappa_e - SP}{\kappa_e - EO}$
Water:												
Cell IV.....	53	0 6	3 0	765	-92	135	6 3	681	-162	1.76	0.89	2.12
Cell III.....	20	0 6	4 1	346	-68	20	4.1	769	-134	1.97	2.22	1.00
Cells III and IV.....	73	0 6	3.27	650	-85	155	6 0	693	-158	1.86	1.07	1.84
KCl												
$10^{-4} N$	10	14 89	14.1	132	-79	4	11 2	95 0	-45	0 57	0.72	0 79
$5 \times 10^{-4} N$	6	70 68	108.9	11 2	-52	4	55 8	18.5	-44	0 85	1 65	0 51
$10^{-3} N$	8	139 99	116 7	9 9	-49	4	118 2	8 0	-40	0 82	0 81	1 01
BaCl ₂												
$10^{-4} N$	8	13.47	11.6	77.9	-38	4	12 9	62.2	-34	0 89	0 80	1.11
$5 \times 10^{-4} N$	8	64.87	51.4	12 4	-27	4	58.2	11.8	-29	1 08	0.95	1 13
$10^{-3} N$	2	127 59	112 3	4.8	-23	4	125 1	5 3	-28	1 22	1 11	1.11
AlCl ₃												
$10^{-3} N$	7	1.98	1 51	722	-46	4	2 40	318	+32	-0 70	0 44	1 59
$5 \times 10^{-3} N$	2	7.37	3 70			4	6 81	138	+40			1 84
$10^{-4} N$	3	14.16	13 8	70 9	+41	4	10 3	80	+34	0 83	1 13	0.75
$5 \times 10^{-4} N$	4	68 06	61 0	15 7	+40	4	62 3	16 6	+42	1 05	1 06	1 02
$10^{-3} N$	2	135 56	118.4	7 0	+35	4	116 4	8 1	+40	1 14	1 15	0.98
Mean for electrolytes										0 94	1 04	0 93

3.28/2.46 (1.6 to 1.3) if an empirical value of the cross section is calculated from the observed V/P ratios, and (2) that both the electrosmosis and the streaming potential ζ -potentials will be multiplied by the *same* factor since both sets of values depend on the cross section, Q , in the same way. The V/P discrepancy does not therefore invalidate our general conclusions regarding the relative values of the ζ -potential obtained from electrosmosis and from streaming potential experiments.

COMPARISON OF ZETA POTENTIALS OBTAINED FROM ELECTROSMOSIS AND FROM STREAMING POTENTIAL MEASUREMENTS

The principal results of our experiments with water and with electrolyte solutions are summarized in table 5 for the purpose of comparison. The ζ -potentials calculated from these are plotted in figure 4.

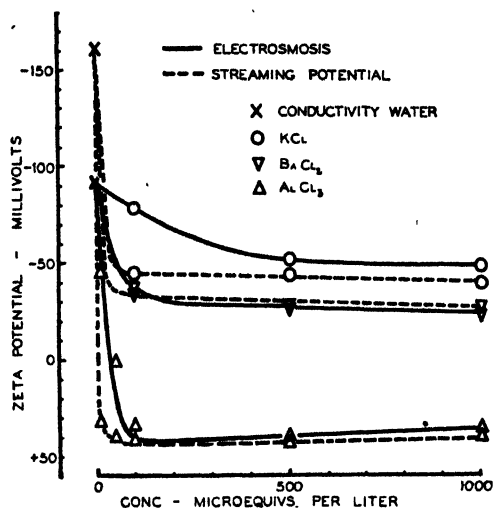


FIG. 4. Comparison of electrokinetic potentials obtained from electrosmosis and streaming potential measurements

The results of the experiments with conductivity water show a striking discrepancy in the ζ -potentials obtained from the two types of electrokinetic measurement, the electrosmosis values (-162 millivolts with cell IV and -134 millivolts with cell III) being almost twice as great as the streaming potential values (-92 millivolts and -68 millivolts with cells IV and III, respectively), the differences being well outside of the experimental error.

Such a difference in the ζ -potentials is not intrinsically a contradiction of the Helmholtz equations, for the following reason. These equations imply that—whatever the charge distribution in the electrical double layer—under the influence of an applied electrical field parallel to the wall

(electrosmosis) or of a mechanical force (streaming potential), a lateral displacement of a mobile part of the double layer takes place relative to a sessile part fixed on the wall, and that somewhere very close to the wall there exists a limiting plane of shear where the lateral velocity of the liquid with respect to the wall is zero. The difference in the electrical potential at this distance from the wall and that in the interior of the solution is the zeta potential. The ζ -potentials calculated from the results of electrosmosis and streaming potential experiments will be identical only if the limiting planes of shear lie at the same distance from the wall in the two cases. There is no stipulation in the Helmholtz formulation that this condition shall be satisfied.

We had indeed looked for some difference in the two ζ -potentials as an indication that the condition may actually not be satisfied. The discrepancy actually observed does not, however, allow a definite conclusion of this sort to be drawn, because of a certain internal inconsistency in our own results. The large ratio of the ζ -potentials obtained from the forty experiments with cell III corresponds, as it should, to a similar ratio of the quantities E/P and V/I and an equality of the observed apparent conductivities of the liquid in the slit. In the one hundred eighty-eight experiments with cell IV, however, we find a similar high ratio of the ζ -potentials coupled with practical equality of the ratios E/P and V/I . This is an apparent contradiction of the usual assumption that equality of E/P and V/I indicates equality of the ζ -potentials.

The discrepancy is explained when we compare the measurements of the apparent slit conductivity made during the two sets of experiments and note that the value of κ_s observed in the streaming potential experiments was twice as great as that measured in the electrosmosis experiments, although the procedures were identical and the bulk conductivities of the water were practically the same in both cases.⁵ Although the inconsistency noted robs our results of some of their theoretical import, it serves to point a warning that mere equality of the quantities E/P and V/I does not in itself demonstrate equality of the ζ -potentials without definite experimental proof that the specific conductances of the liquid in slit, capillary, or diaphragm are identical.

Identity of ζ -potentials obtained from experiments with electrolyte solutions

The results of the experiments with electrolytes show on the whole that ζ -potentials obtained from streaming potential measurements were identical with those obtained from electrosmosis measurements. They there-

⁵ This increase in ζ with increase in the specific conductance of the slit liquid is in the reverse direction from the effects noted by Lachs and Biczuk (14) with conductivity water, but is consistent with the initial rise in the ζ -concentration curve commonly observed in electrokinetic experiments.

fore point to the conclusion that the applied mechanical force acting on the liquid in the streaming potential experiment displaces the same fraction of the double layer as the applied electrical force in electrosmosis acting directly on the charged ions in the layer. The observed equality in the values of ξ is not a fortuitous result of a particular choice of applied field (electrosmosis) or of applied pressure (streaming potential), since the ξ -potentials were found to be independent of these factors.

Anomalous reversal of sign of the ξ -potential

The conclusion just stated rests on a comparison of the average values of all experiments with the three electrolytes. When we consider the individual experiments at different concentrations, we find random variations such as are generally observed in similar work. The usual valence effects are observable, including charge reversal in the case of solutions containing the trivalent Al^{+++} cation.

The most surprising result of all our work with electrolyte solutions was the observation that the electrosmosis and the streaming potential effects *were of opposite sign* in the measurements with $10^{-5} N$ aluminum chloride solution; that is, the direction of electrosmosis corresponded to a negative ξ -potential (-46 millivolts), while the streaming potential corresponded to a positive ξ -potential ($+32$ millivolts). This was so important a result that in order to establish the reality of the effect we disconnected the pressure apparatus just after completing the streaming potential measurement and immediately made another electrosmosis measurement. Electrosmosis again occurred as before in the direction corresponding to a negative ξ -potential. We are therefore forced to recognize that conditions may exist in an electrokinetic system where electrokinetic effects may differ not only in magnitude but even in sign. This suggests that in the neighborhood of the electrokinetic isoelectric point, where charge reversal takes place, the electrical double layer may have a complex structure involving several layers of charge of alternately positive and negative sign, as has been proposed by several writers (8, 9, 17). To complete the explanation of the effect we have observed it is necessary to suppose that when the tangential mechanical force was applied to such an interfacial layer in the streaming potential experiment, the limiting plane of shear (the "rigidity boundary" of Müller (18)) lay in a different part of this complex double layer than when the electrical force was acting in the electrosmosis experiment. That is, the rigidity boundaries in the two experiments lay in regions of the double layer where the electrical potential was of different sign.

SUMMARY

1. Electrosmosis and streaming potential measurements have been made with an optically polished glass slit in contact with conductivity water and

with solutions of electrolytes of different valence types. The measurements were made over the concentration range of 10^{-3} *N* down to about 10^{-6} *N* (conductivity water),—that is, the range in which electrokinetic effects change most rapidly with concentration.

2. The values of the ζ -potential for the glass-water interface were calculated from the results of these experiments. The electrokinetic potentials thus obtained from the electrosmosis experiments were nearly identical with those calculated from the results of the streaming potential measurements over most of the concentration range studied.

3. However, in the region of extremely low ionic concentrations large discrepancies were found. With water of specific conductance 0.6×10^{-6} mho per centimeter the streaming potential effects were relatively almost twice as great as the electrosmotic effects. The interpretation of the results, however, is complicated by the discrepancy in the observed values of the apparent specific conductance of the liquid in the slit.

4. With aluminum chloride solution of concentration 10^{-5} *N* a remarkable result was obtained when it was observed that the electrokinetic effects of electrosmosis and of streaming potential were of opposite sign, the values of the ζ -potential being respectively -46 millivolts and $+32$ millivolts. The two experiments were made in immediate succession without any reasonable chance for a change in the structure of the electrical double layer.

We wish to acknowledge with thanks the grant of funds by the American Association for the Advancement of Science for the purchase of the Comp-ton electrometer used in this work.

REFERENCES

- (1) ABRAMSON, H.: J. Am. Chem. Soc. **50**, 390 (1928).
- (2) ABRAMSON, H., AND GROSSMAN, E. B.: J. Gen. Physiol. **14**, 563 (1931).
- (3) BENGOUGH, G. D., STUART, J. M., AND LEE, A. R.: J. Chem. Soc. **1927**, 2156.
- (4) BRIGGS, D.: J. Am. Chem. Soc. **50**, 2358 (1918).
- (5) BULL, H. B.: Colloid Symposium Monograph **11**, 577 (1934).
- (6) BULL, H. B.: Kolloid-Z. **66**, 20 (1934).
- (6a) DAVIES, S. J., AND WHITE, C. M.: Proc. Roy. Soc. London **119A**, 92 (1928).
- (7) ETTISCH, G., AND ZWANZIG, A.: Z. physik. Chem. **147A**, 151 (1930).
- (8) EUCKEN, A.: Z. physik. Chem. **1B**, 375 (1928).
- (9) FREUNDLICH, H.: Kapillarchemie, 4th edition, Vol. 1, p. 357. Akademische Verlagsgesellschaft, Leipzig (1930).
- (10) FREUNDLICH, H., AND ABRAMSON, H.: Z. physik. Chem. **133A**, 51 (1928).
- (11) GRUMBACH, A.: Ann. chim. phys. [8] **24**, 451 (1911).
- (12) KANAMARU, K.: Cellulose Ind. **7**, 3-16, 29-52 (1931); Abstracts, 3-13 (in English); Chem. Abstracts **25**, 3895 (1931).
- (13) KÖHLER, G.: Z. physik. Chem. **157A**, 113 (1931).
- (14) LACHS, H., AND BICZYK, J.: Z. physik. Chem. **148A**, 441 (1930).

- (15) MCBAIN, J. W., PEAKER, C. R., AND KING, A. MILLICENT: J. Am. Chem. Soc. **51**, 3294 (1929).
- (16) MANEGOLD, E., AND SOLF, K.: Kolloid-Z. **55**, 273 (1931).
- (17) MUKHERJEE, J. N.: Trans. Faraday Soc. **16**, 103 (1921).
- (18) MÜLLER, H.: Cold Spring Harbor Symposia on Quantitative Biology **1**, 1 (1933).
- (19) QUINCKE, G.: Pogg. Ann. **113**, 513 (1861).
- (20) REICHARDT, H.: Z. physik. Chem. **154A**, 337 (1931).
- (21) REICHARDT, H.: Z. physik. Chem. **159A**, 417 (1932).
- (22) REICHARDT, H.: Z. physik. Chem. **166A**, 433 (1933).
- (23) SAXÉN, U.: Wied. Ann. **47**, 46 (1892).
- (24) THON, N.: Z. physik. Chem. **147A**, 147 (1930).

A STUDY OF SOME PHYSICAL PROPERTIES OF FLOUR DOUGHS IN RELATION TO THEIR BREAD-MAKING QUALITIES

P. HALTON¹

Research Association of British Flour Millers, St. Albans, England

AND

G. W. SCOTT BLAIR

Department of Physics, Rothamsted Experimental Station, Harpenden, England

Received April 3, 1935

INTRODUCTION

Attempts to measure the physical properties of flour doughs were made by Kosutány (4) as early as 1907. This author pulled out a cylinder of flour dough at a constant rate, and measured the stress build-up.² Although not clearly distinguishing between viscous and elastic properties, the author's interpretation of his data points clearly to a number of the conclusions reached in the present work.

It is curious that this valuable work, in which Kosutány came so near to separating and measuring specific physical properties, should have lain fallow for so many years. From 1907 to 1932 work on the physical properties of flour doughs was confined almost entirely to the production of instruments measuring a complex mixture of properties, which, although in some cases of real value in the bread-making industry, threw little or no light on the physical nature of the problem. In 1932-33 three papers were published by Schofield and Scott Blair (8), in which certain of the physical properties of doughs were separated and independently measured. For the sake of convenience these papers will be referred to as I, II, and III.

In paper I it was emphasized that flour dough belongs to a group of materials in which a high degree of plasticity is combined with considerable elasticity. When under stress the relative amounts of plastic (non-

¹ By mutual agreement the authors' names are in alphabetical order and no seniority is implied.

² Terzaghi (9) develops very similar ideas. The constant which he calls "degree of elasticity" (p. 79) is closely connected with relaxation time (*vide infra*). Terzaghi's work refers to soils and clays, but their behavior is in some ways strikingly similar to that of flour doughs. See also a recent paper by M. P. Wolarowitsch and K. I. Samarina (10) dealing with some physical properties of flour doughs.

recoverable) and elastic (recoverable) deformation depend on the time of duration of the stress. An extended significance was given to Maxwell's relaxation time, so that the equation

$$t_r = \eta/n$$

in which t_r = relaxation time, η = viscosity, and n = shear (rigidity) modulus,³ could be applied to a material such as flour dough, in which neither η nor n is a constant.

It was found that η and t_r decrease with increasing stress and increase with increasing deformation. Fall in viscosity with increasing stress is a phenomenon well known in many colloidal systems, and has been called "structural viscosity" (6). Increase in viscosity with increasing strain is a common characteristic of metals, and is called "work-hardening."

In paper II, these two properties were more fully studied by observing the rate of shear of cylinders of dough hung vertically, and allowed to elongate under the action of gravity (the method of rheograms).

The Maxwell equation could only be tested satisfactorily after the most suitable value of modulus to use in calculating viscosities from relaxation times was known. Experiments to decide this point were described in paper III, and agreement was found to be as satisfactory as could be expected when the best value for the modulus was used. These experiments also made it clear that dough shows two other properties characteristic of metals, namely, elastic hysteresis and elastic after-effect.

The former causes the rigidity modulus to fall slowly as stress is raised, and also as stress is lowered, but at the point at which the sign of dS/dt changes,⁴ the modulus increases abruptly. The latter means that elastic deformations are not recovered instantly, so that unless time is given for slow recovery to take place, certain deformations will be regarded as permanent which are in reality recoverable. This would lead to considerable errors in determining viscosity and modulus (see experimental section). In view of the partial understanding which this treatment had already given, it seemed advisable to investigate further the relationship between these fundamental physical properties, and those qualities of the dough which are of importance in the bread-making industry. For this purpose the Physics Department of the Rothamsted Experimental Station and the Research Association of British Flour Millers decided to coöperate in the further study of the problem.

³ Note that for flour doughs, Poisson's ratio being 0.5, we can assume the rigidity modulus to be equal to one-third of Young's modulus. The shearing stress likewise is one-third of the loading stress. In the present paper, the term "rigidity modulus" is often abbreviated to "modulus," since no other modulus is discussed.

⁴ Where S is shearing stress and t the time.

The general principles have now been elucidated, and although much detail requires yet to be filled in, the present paper gives a description of the conclusions to date.

EXPERIMENTAL

By far the most serious difficulties that have been encountered were those associated with the reproducibility of measurements on different test pieces from the same dough. In papers I, II, and III accurate replication on different test pieces was not attempted, and although the phenomena described could be repeatedly observed, it was realized that no fully satisfactory technique existed for such replication. In the course of the present investigation much time has been spent in developing such a technique, and the method finally adopted has proved on the whole to be satisfactory.

TABLE 1

The effect of mixing on the viscosity and modulus of the dough

TIME OF MIXING	TIME OF RESTING AFTER MIXING	VISCOSITY*	MODULUS*
<i>minutes</i>	<i>minutes</i>		
3	0	6.38×10^6	4.29×10^4
	30	4.92×10^6	3.94×10^4
	60	4.04×10^6	3.73×10^4
12	0	2.92×10^6	3.02×10^4
	30	3.55×10^6	3.41×10^4
	60	3.51×10^6	3.50×10^4

* All data for viscosities (η) and moduli (n) in this paper are given in c.g.s. units, but it must be borne in mind that they refer only to arbitrary fixed conditions of stress and strain.

It is necessary to make as homogeneous a dough as possible, and it has been found that machine mixing of the flour and water gives the most satisfactory results. The longer the time of mixing, the more homogeneous is the finished dough, but excessive mixing has a very marked effect on the dough's physical properties.

From the data in table 1 it can be seen that excessive mixing considerably lowers the viscosity and modulus of the dough, but that these increase again on resting. Such treatment, however, permanently lowers the tensile strength of the dough.

It will be shown later that the general tendency on aging a dough is for the viscosity and modulus both to fall. It is only after prolonged mixing that the opposite effect more than compensates for this fall, producing a net rise in both properties. Thus it appears in table 1 that after 3 min-

utes mixing, the effect of standing is the opposite of that produced by 12 minutes mixing.

The sample of dough is transferred from the mixer to a "gun," consisting of a hollow metal cylinder, 5 cm. long and 2.5 cm. in diameter, fitted with a plunger. To the bottom of the cylinder is fitted a solid piece of metal drilled with a hole 3.5 cm. long and 0.5 cm. in diameter. This first gun, into which the dough can be placed by means of a spatula, thus avoiding handling it, is too big to fit conveniently on to the apparatus, and therefore the extended dough cylinder is squeezed straight into a second smaller gun 15 cm. long and 1 cm. in diameter, which is fitted with an end piece similar to that of the first gun. The dough is forced from this second gun straight on to the surface of a bath of mercury.

Statistical analysis⁵ showed that there was no greater error in comparing test pieces from different doughs than in comparing pieces from the same dough. It thus appeared that the chief source of error lay in the method of preparation of the test pieces. It was found that the force applied to the guns very largely affected the physical properties of the prepared dough cylinder. A system of pulleys and weights was therefore used for manipulation of the guns, and, provided that the weights were small, we found very little alteration of the properties of the doughs. The importance of a carefully standardized use of these guns cannot be too strongly emphasized.

During extrusion the dough cylinder swells, this swelling being in general greater for good than for poor quality flours. The exact connection, however, is not clearly understood.

The dough cylinders have been examined by the two general methods described in papers I, II, and III, namely (a) rheograms, and (b) the mercury trough extensimeter, but the technique of the latter method has been extended and developed.

(a) *The rheogram method.* This method has been further developed and has now reached a stage at which the results are excellently reproducible, and, although not free from errors, it provides the most satisfactory way at present available for separating the effects of work-hardening (rise in viscosity with rising strain) and structural viscosity (fall in viscosity with rising stress).

In most doughs these two properties appear, under the conditions of the rheogram experiments, approximately to cancel out. Without committing ourselves to any assessment of the degree of accuracy of individual samples, an examination of the data obtained from a study of some sixty doughs made from a series of twenty different flours, leads to the conclusion that certain flours tend to show higher or lower degrees of work-

⁵ Our best thanks are due to Mr. F. Yates of the Rothamsted Experimental Station Statistical Department for doing this analysis.

hardening than others, and that this property generally persists when different amounts of water and times of aging are used. Such differences do not, however, correlate directly with flour quality, and we conclude that weakness in a flour due to an unsuitable degree of work-hardening is the exception rather than the rule.

Certain practical difficulties are encountered in using the rheogram technique in the case of sticky doughs, and doughs of poor tensile strength. Moreover, both viscosity and rigidity modulus can be calculated from a single test on the extensimeter (*vide infra*); therefore the rheogram method was not employed further in this investigation.

(b) *The extensimeter.* This instrument, which is an improved model of the extensimeter described in papers I and III, is shown diagrammatically in figure 1.

A dough cylinder A, about 10 cm. long by 0.7 cm. in diameter, made as described above, is floated on a mercury bath. The ends of this cylinder are connected by means of cork "chairs" and cotton threads to two small scales B, which are observed through low-power microscopes, C. The

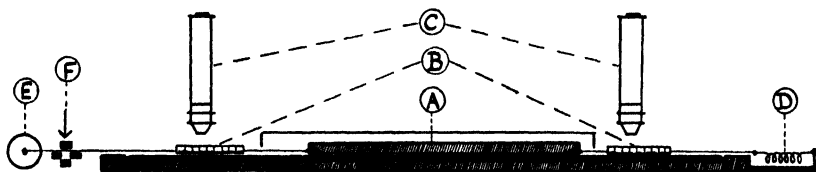


FIG. 1. The mercury bath extensimeter

smallest divisions on the scales are 0.013 cm. in length, and readings to one-tenth of this can be estimated with a fair degree of accuracy. To one scale is fastened a steel spring D, the other end of which is securely attached to the framework of the apparatus; the other scale is connected by cotton to a small winch (E), which can be wound either by hand or by a small motor.

During experiments the dough is protected by a cover, the felt lining of which is damped to provide a humid atmosphere to prevent drying out of the dough surface.

When the winch (E) is wound up, the dough and scales are moved to the left, and this extends the spring D. The dough is therefore subjected to a stress, the value of which is proportional to the extension of the spring, and inversely proportional to the cross section of the dough cylinder. The spring is calibrated by noting the extension caused by hanging weights of various sizes from it when placed in a vertical position. The diameter and initial length of the dough cylinder are measured with calipers.

In order to measure viscosity, which is defined (see paper I) as the ratio

of shearing stress to velocity gradient (i.e., rate of change of non-recoverable strain), we can either fix the rate of change of strain and measure the stress, or fix the stress and measure the rate of change of strain. The latter has in practice been found to be by far the simpler method to use, and has been the basis for most of the experiments described in this paper.

Before doing an experiment, the necessary deflection of the spring to give the desired stress is first calculated from a knowledge of the constant for the spring and the cross section of the dough cylinder. The winch is then rapidly wound up until the shift in the scale attached to the spring corresponds to this required stress. For ordinary purposes we worked with an arbitrary tensile stress of 1500 dynes per square centimeter (shearing stress 500 dynes per square centimeter).

Under stress the dough cylinder extends, and for five minutes this extension is taken up by slowly winding the winch so that the deflection of the right-hand scale is kept constant. By this means the stress is kept almost constant, the rise in stress with slight thinning of the dough cylinder not being generally great enough to introduce any serious error, especially when relative, rather than absolute, viscosities of doughs are required.

By measuring the extension at minute intervals it would appear that the mean viscosity for each minute could be determined, and from this an indication of the amount of work-hardening (i.e., change in viscosity with strain) assessed. This is not, however, practicable, since elastic after-effect is taking place during the whole process (see introduction).

The stress is released at the end of the five minutes and the dough allowed to relax until no further change in length takes place (this takes about three to five minutes). The difference in the length of the dough cylinder before any stress is applied to it and at the end of relaxation gives a measure of the non-recoverable strain caused by the stress acting for five minutes.⁶ From this a mean viscosity can be determined by dividing the non-recoverable strain per unit time into the stress. This is free from errors due to elastic after-effect.

The amount of recoverable or elastic deformation is obtained by noting the change in length of the dough cylinder between the time of releasing the stress and the end of relaxation. The value of the shear modulus which is given by the ratio

$$\frac{\text{change in shearing stress}}{\text{change in recoverable strain}}$$

⁶ Strictly speaking, the strains should be calculated from $\log_e l/l_0$, as in the rheogram calculation, but for the small strains used the method described here is adequate.

is a *mean* value for a change in stress from 500 to 0 dynes,⁷ the modulus falling progressively during the lowering of the stress due to elastic hysteresis (see introduction).

Effect of temperature

Experiments have shown that the viscosity of a typical dough falls by about 10 per cent per degree Centigrade rise in temperature and the modulus by about 5 per cent. This makes it desirable to exercise careful control over the temperature. The extensimeter is not easily thermostated, and, moreover, the processes of dough preparation should also be carried out at a constant temperature. It would thus be best to carry out all measurements in a constant temperature room.⁸

Although a suitable constant temperature room has now been built, the fact that it was not available for the earlier work meant that we could only make direct comparison between results obtained over periods during which laboratory temperature did not fluctuate very widely, and in consequence we have had to forego making as full use of our data as we should otherwise have been able to do. Further, since the viscosity falls about twice as fast (with rise in temperature) as does the modulus, it is clear that the all-important⁹ viscosity modulus ratio (relaxation time) is higher, the lower the temperature. This supports the view held by some bakers that dough should be fermented and put into the oven at as low a temperature as is consistent with the satisfactory working of the yeast.

The temperature coefficients also vary with the age of the dough, and it is thus clear that the temperature at which it is aged plays an important part in defining its physical properties at any given time, and hence in determining the quality of the resulting bread. Further experiments are needed to explore this field.

WATER ABSORPTION

When determining the value of a flour in the bakehouse the first step is to turn it into dough by mixing with water and other ingredients. The baker does not use a constant ratio of flour to water for all samples, otherwise some of his doughs would be too soft and sticky, while others would be too tough, extremes of condition which not only cause serious difficulties in the handling of the doughs, but which do not result in bread representative of the value of the flour. In view of this, the baker varies the

⁷ The stress is never allowed to fall quite to zero, owing to the necessity for keeping the cotton taut, but the final stress is very small, and is the same in all experiments.

⁸ Care must be exercised to ensure proper ventilation and so prevent the danger of mercury poisoning (see Stock (9)).

⁹ See later, under the section headed "general considerations."

amount of water he adds to each flour so that his doughs are easy to handle and in general bake into as good quality bread as his various flours are capable of making.

We are therefore faced with the problem of determining the significance of this optimum amount of water, or "water absorption" as it is called in the bakehouse, and also with the necessity of determining some method whereby it could be fixed. In assessing water absorption the baker relies on his sense of touch, and one of the impressions which helps in his judgment of correct absorption is the extent to which the dough sticks to his hands.¹⁰

It appeared to us that the baker made up his doughs so that the stickiness was just short of being a trouble, and on this assumption we based our

TABLE 2

Effect of water content on viscosity and modulus of flour doughs

FLOUR	WATER CONTENT				
	- 1 gal.	- $\frac{1}{2}$ gal.	Normal	+ $\frac{1}{2}$ gal.	+ 1 gal.
No. 1 Manitoba:					
Viscosity ($\times 10^6$)	10.0	7.5	5.8	4.8	4.1
Modulus ($\times 10^4$)	4.1	3.6	3.1	2.6	2.1
Barusso Plate:					
Viscosity ($\times 10^6$)	15.0	8.3	5.7	4.4	3.5
Modulus ($\times 10^4$)	4.6	4.0	3.4	2.8	2.2
Australian:					
Viscosity ($\times 10^6$)	7.5	4.8	3.5	2.8	2.3
Modulus ($\times 10^4$)	5.5	4.6	3.6	2.6	1.6

Normal absorptions: No. 1 Manitoba, 15.6 gals. per sack; Barusso Plate, 15.3 gals. per sack; Australian, 14.0 gals. per sack.

first attempt to connect water absorption with a physical property, so that by the measurement of the latter we could fix the former.

Measurements of stickiness were made by measuring the force required to overcome the adhesion of a metal weight to the surface of a dough. The method used was a modification of those proposed by Kachinski (3) and others (1, 2, 5, 7) for measuring the stickiness of soils. It has, however, not been possible to make the measurements reproducible enough to use as a means of assessing water absorption.

The connection between water content and two other physical properties, namely, viscosity and rigidity modulus, was next investigated.

For this a series of flours was obtained, and from each flour several doughs were made containing different amounts of water. The data

¹⁰ For experiments on the psychological aspect of stickiness, see Zigler (12).

obtained by measuring the viscosities and moduli of the doughs made from three of these flours, a No. 1 Manitoba, a Barusso Plate, and an Australian are given in table 2.

Each flour was examined at the absorption chosen in the bakehouse which we have called "normal," and at four other water contents $\pm \frac{1}{2}$ gallon and ± 1 gallon per 280-lb. sack of flour.¹¹ Each dough was fermented for four hours, at the end of which time samples were taken for viscosity and modulus measurements. In figure 2 curves are drawn showing the relationship between these two properties at each of the five water contents for each of the three flours.

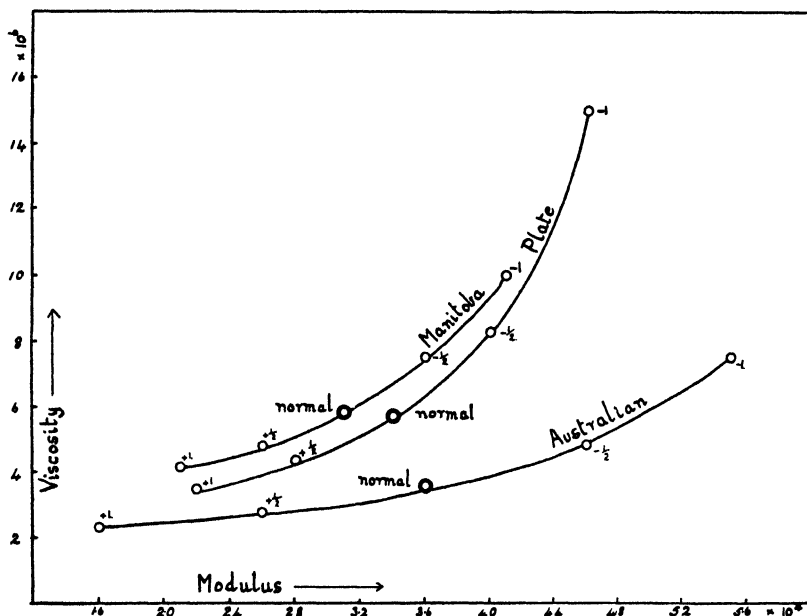


FIG. 2. The effect of water content of dough on the viscosity and modulus

An examination of these curves shows that with each flour both viscosity and modulus fell with increasing water content and vice versa. The relative effects on these two properties were not the same, and differed from flour to flour. The effects of a change of 2 gallons in water content on viscosity and modulus are given in table 3, the figures representing the difference in values for the driest and wettest doughs expressed as a percentage of the average.

These figures show that the effect both on viscosity and modulus was least in the case of the Manitoba, which is in keeping with the experience

¹¹ One gallon per sack = 3.57 per cent on the flour.

of the baker that this type of flour has a much greater tolerance to changing water content than any other. The Plate flour differed from the Manitoba chiefly on account of the much greater effect of changing water content on viscosity, while in the case of the Australian both viscosity and modulus, and particularly the latter, were more markedly affected than in the case of the Manitoba. It is probable that a big upward change in viscosity with decreasing water content is of much less account in the bakehouse than a big increase in modulus, as the latter would make the doughs "dead" and lifeless (see later).

The three doughs of particular interest are the "normal" doughs, and it will be noticed that these doughs differed very considerably in viscosity, but only to a small extent in modulus. It is probable that the baker is unconsciously more influenced in choosing his water absorption by the moduli of his doughs than by their viscosities, and in consequence we may be able to use measurements of the former property as a means of determining correct water absorption. This point, however, needs much further investigation before it can be settled.

GENERAL CONSIDERATIONS

Although it is quite possible to make a dough from any flour whatsoever so that it shall have any desired viscosity or modulus (within wide limits), by using the appropriate amount of water, it is well known that a poor flour cannot by any such means be made to give a dough of satisfactory plastic and elastic properties. The reason for this is clearly seen from table 3. It is here apparent that if a "strong" flour dough (Manitoba) is compared with a "weak" (Australian) at the same viscosity, the modulus of the strong flour is much lower than that of the weak. If the comparison is made at the same modulus value, the strong flour has by far the greater viscosity. The intermediate Plate flour falls between the two extremes. This suggests that the relaxation time (η/n , see paper I) is of primary importance. This suggestion has been amply verified. It is, of course, clear that we cannot regard relaxation time as a constant of a dough, since it varies with both stress and deformation, but it has become increasingly evident during the course of this work that if doughs are compared under similar conditions of stress and strain, and if these conditions approximate as closely as possible to those obtained in the commercial dough, a comparison of relaxation times ("viscosity-modulus ratios") gives a primary measure of the differences in flour quality (although as is shown later, many other factors have to be taken into consideration as well). In paper I it is suggested that "the dough contains elastic elements which form a connected structure . . . (which elements) are not joined securely, but slide past one another whenever a sufficient stress is operative. The viscosity which has been determined is mainly governed by the behaviour

of a plastic film by which the elastic elements are connected. It is quite possible that the elements are capable of complete elastic recovery, but there is at present no criterion for testing this. The time of relaxation is a characteristic of the connected structure as a whole and its value is as much determined by the elasticity of the elements as by the viscosity associated with their plastic junctions. . . . In relating these deductions to the known structure of the dough, one may safely identify the elastic elements with the protein part of the flour."

When a dough rises under the action of yeast, it is advantageous for as high a percentage as possible of the deformation to be elastic (recoverable). Non-recoverable deformations imply flow of the cell-walls, leading to their rupture, and collapse of the dough due to inability for it to hold its shape, resulting in a loaf having large and badly shaped holes, a poor volume, and bad over-all shape. Big elastic extension resulting from low modulus tends to produce a big rise when the dough is first placed in the oven, and hence big loaf volume.

TABLE 3
Effect of change in water content

	MANITOBA	PLATE	AUSTRALIAN
Viscosity	83	124	106
Modulus.	64	70	105

The property by which an extended dough on release recovers a high percentage of its extension, is called by bakers "spring." It is clear that the extent to which the dough fails to return to its original length after such an extension will depend on how far the elastic elements have slipped past one another. This depends on the amount of friction between them, which, as we have seen, corresponds to the viscosity of the dough (as normally measured). The higher the viscosity, the less the slippage. But the amount of slippage depends not only on the viscosity, but also on the internal stress set up in the elastic elements. If we think of these as coiled springs, it is easy to see that the "lighter" the springs (i.e., the lower their moduli), the less stress will be built up for any given extension, and hence the less will be the slippage for a given viscosity. Thus a dough showing good "spring" will have a relatively high viscosity and low modulus, whereas a dough having bad spring will have a relatively low viscosity and high modulus.

It is now clear why the baker attaches so much importance to "spring" in his doughs. Good spring means a high viscosity modulus ratio (big relaxation time), and, as already stated, this is (other things being equal) the primary characteristic of a good flour.

It is pertinent to enquire as to the significance of the extent of the variation of viscosity and modulus with stress, strain, and stress history for different flours. Experiment has shown that even widely different flours show a very similar degree of elastic hysteresis, and no marked differences in their elastic after-effect behavior. As explained in paper III elastic after-effect is important in that unless attention is paid to eliminate its effect, it is liable to interfere seriously with the correct determination of viscosity.

TENSILE STRENGTH

In the bakehouse occasional doughs are encountered which "tear" badly during the baker's manipulation and during the rising of the doughs under the pressure of the gas generated inside them. Such doughs are said to be "short" and bake into unsatisfactory bread. Owing to the tearing, excessive gas leakage occurs which results in poor loaf volume, and the actual tearing gives the outside of the loaf a ragged appearance. In addition, the insides of such loaves easily crumble when pressed with the fingers. It thus appears that for such flours tensile strength is also a factor of major importance. This property is now being investigated.

AGING AND FERMENTATION OF DOUGHS

In the process of bread making the doughs are kept for some hours before baking into bread. Not only do their handling properties depend on the length of this period, but the type of bread also shows considerable variation.

In order to determine the changes with age in the physical properties of such doughs, and to find what connections exist between these changes and bakehouse behavior, a series of flours was obtained which had been previously examined by the baker. The doughs were made up with the same ingredients as had been used in the bakehouse and were kept at 27°C., samples being taken at hourly intervals for viscosity and modulus measurements, which were made at room temperature.

The data obtained on four of these flours, a No. 1 Manitoba, a No. 3 Manitoba, a Barusso Plate, and a South Australian, are given in table 4, and curves drawn from these data are given in figures 3, 4, and 5.

It will be noticed that no data are given for freshly made doughs. This is because of the difficulty of obtaining reproducible measurements on them. Rapid changes take place during this initial period and are probably connected with the rate of absorption of water by the flour. After one-half to one hour these effects disappear, and the physical properties then change in a normal and regular fashion.

In the case of the above four flours, the changes in physical properties were almost linear functions of time.

TABLE 4

Effect of fermentation on viscosity, modulus, and the η/η ratio

FLOUR	TIME IN HOURS	VISCOSITY $\times 10^6$	MODULUS $\times 10^4$	η/η RATIO
No. 1 Manitoba	1.23	3.97	3.16	126
	2.12	3.82	3.02	126
	3.05	3.79	3.21	118
	4.93	3.32	2.99	111
	6.00	3.27	3.21	102
	6.93	3.25	3.09	105
No. 3 Manitoba	1.10	3.25	2.61	124
	2.03	2.84	2.37	120
	3.08	2.68	2.53	105
	5.02	1.88	2.18	86
	6.07	2.04	2.18	93
	7.03	1.83	2.03	90
Barusso Plate	1.18	3.33	3.53	94
	2.03	3.46	3.47	100
	3.13	2.83	3.23	87
	5.02	2.56	3.08	83
	6.00	2.45	2.76	89
	7.07	2.07	2.39	89
Australian	1.07	2.52	3.21	78
	2.05	2.18	2.92	74
	3.00	1.97	2.82	70
	5.00	1.39	2.32	60
	6.13	1.00	2.06	48
	7.00	0.76	1.58	48

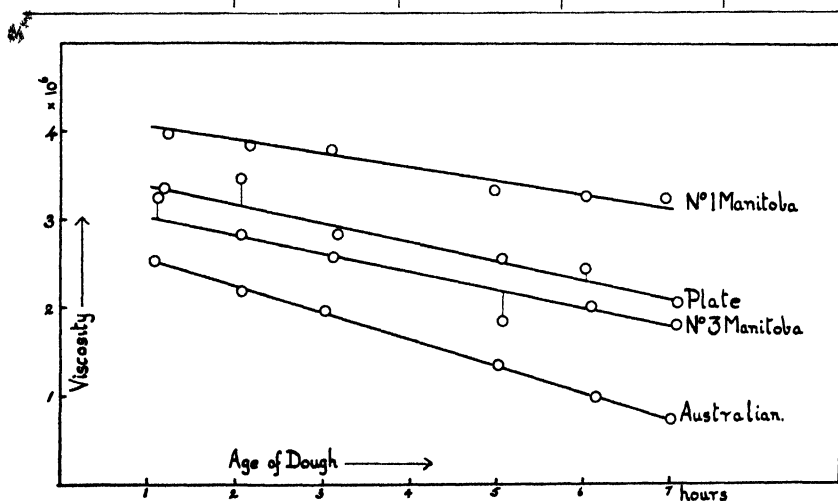


FIG. 3. The effect of age of the dough on the viscosity

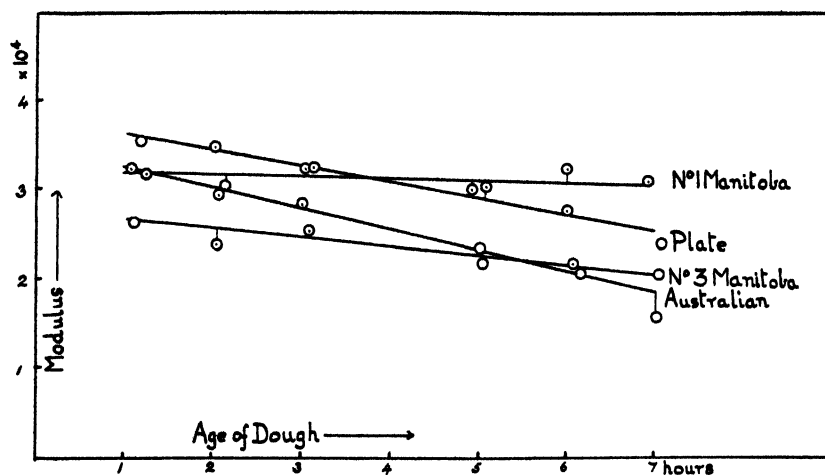


FIG. 4. The effect of age of the dough on the modulus

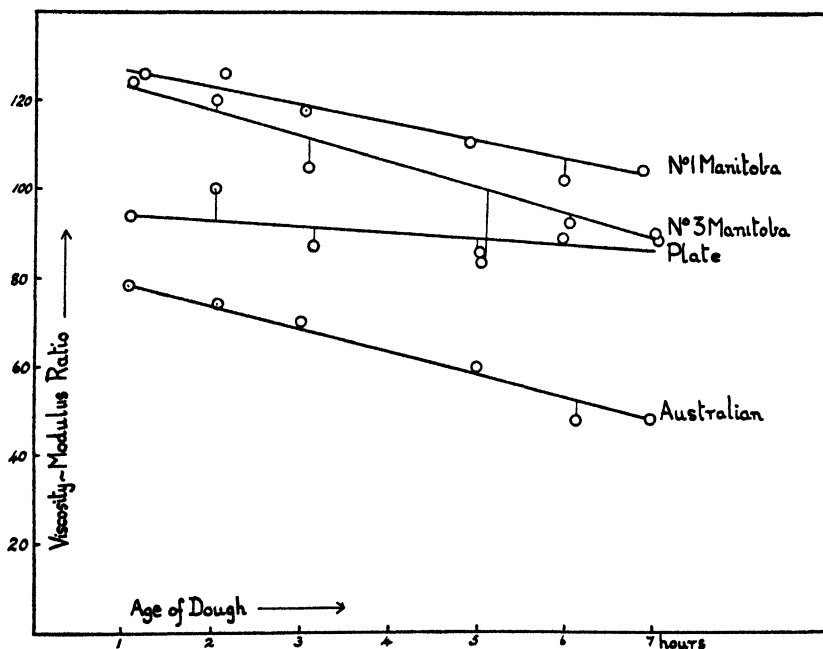


FIG. 5. The effect of age of the dough on the viscosity-modulus ratio

The data given in table 5 have been obtained from the curves (see figures 3, 4, and 5). An examination of the data shows that both viscosity and modulus fell with time of fermentation, and that in the case

of each flour the viscosity fell more rapidly than the modulus, resulting in the ratio of these two properties also falling with increasing time.

In attempting to correlate these changes with the changes which took place in the handling properties of the doughs in the bakehouse, we were at once confronted with the fact that the baker reported that the No. 1 Manitoba dough improved in body and spring as fermentation progressed, that the Plate remained unchanged, and that the No. 3 Manitoba and Australian doughs became softer with increasing time.

TABLE 5
Change in physical properties with time

FLOUR	VISCOSITY AT		ACTUAL DECREASE	PERCENT-AGE DECREASE
	1st hr.	7th hr		
No. 1 Manitoba	4.05×10^6	3.17×10^6	0.88×10^6	22
No. 3 Manitoba	3.01×10^6	1.83×10^6	1.18×10^6	39
Plate	3.37×10^6	2.12×10^6	1.25×10^6	37
Australian	2.84×10^6	0.77×10^6	2.07×10^6	70

FLOUR	MODULUS AT		ACTUAL DECREASE	PERCENT-AGE DECREASE
	1st hr	7th hr		
No. 1 Manitoba	3.19×10^4	3.05×10^4	0.14×10^4	4
No. 3 Manitoba	2.66×10^4	2.04×10^4	0.62×10^4	23
Plate	3.62×10^4	2.55×10^4	1.07×10^4	30
Australian	3.23×10^4	1.87×10^4	1.36×10^4	42

FLOUR	VISCOSITY-MODULUS RATIO AT		ACTUAL DECREASE	PERCENT-AGE DECREASE
	1st hr	7th hr		
No. 1 Manitoba ...	127	104	23	18
No. 3 Manitoba ..	123	89	31	28
Plate	94	87	7	7
Australian	79	48	31	39

This improvement or toughening is associated by bakers with good quality. Several flours which have shown this response to fermentation in the bakehouse have been examined in the laboratory, and in every case both viscosity and modulus have been found to decrease with aging; in fact, no flour has yet been examined which showed a rise in either property during fermentation. It has been noticed, however, that those flours which have been reported as toughening in the bakehouse, were those which showed the smallest fall-off in physical properties when examined in the laboratory.

In the actual stretching of the dough during hand manipulation by the

baker, dough does toughen,¹² but this happens with all flours, and in addition the effect disappears on resting. The toughening the baker speaks of in connection with good quality flours only, is considered by him to be due to the action of fermentation.

Careful tests have now been carried out in the bakehouse in which freshly made doughs were compared with fermented doughs made from the same Manitoba flour, which the baker considered had toughened. When the doughs were moulded side by side, one in each hand, and then allowed a few minutes to rest, it was reported by the baker that when tested by "feel" the older dough was very slightly the softer. It thus appears that bakers have been mistaken in their impressions that certain doughs toughen during fermentation.

When a series of replicate doughs is made from the same flour and allowed to ferment for varying times, it is found that with increasing time the volume and crumb quality of the bread at first improves, and then falls off. This improvement is considered by the baker to be due to what is called the "ripening" of the dough, the actual time to obtain maximum improvement varying with the amount of yeast, and with the type of flour used. "Strong" flours like Manitoba require much longer fermentation for optimum results than "weak" flours like English or Australian. Increasing the amount of yeast in the dough decreases the time of ripening.

Since viscosity, modulus, and relaxation time all fall consistently as the dough ages, it is difficult to explain the initial improvement in bread quality with time of fermentation in terms of the changes taking place in these physical properties.

The decrease in rigidity modulus with time is in itself desirable, but since it is the ratio of viscosity to modulus which is of primary importance in determining flour quality, the general result would be expected to be a fall-off, and not an improvement in bread quality. Also, if a fall in both of these physical properties were desirable, then a similar improvement in bread quality to that which takes place with fermentation could be brought about by using more water in the dough. This is not so, and even when the baker adds too much water to the flour, he still gets an improvement in bread quality with increasing fermentation time.

Although this improvement or "dough ripening" may be partly due to changes taking place in some physical property other than viscosity or modulus, it is possible to account for it on purely mechanical lines. Before a good loaf can be made, the necessary cell structure has to be built up in the dough, and this cell structure must be determined by the number and distribution of the yeast cells. Now normal bakehouse mixing is comparatively crude, and in consequence this distribution is probably anything

¹² See paper II, figure 6.

but uniform. Owing to the activity of the yeast, however, the dough swells, and this probably helps to spread the yeast cells. In addition, at various stages of fermentation, the baker knocks the gas out of the dough and moulds it up, thus again helping towards more uniform distribution. During fermentation the yeast cells multiply, and thus as time goes on the gas-producing centers increase in number.

If the above picture is correct, and it is the building up of the necessary cell structure which determines how much fermentation is required for any flour to give its best bread, then it should be possible to cut down this time by the use of more yeast and/or thorough mixing. That this is so is well known, and it has moreover been verified experimentally by us.

During fermentation we therefore have two processes going on side by side, an improvement due to the multiplication and better distribution of the yeast, and a falling-off in bread-making quality due to the decrease in value of viscosity and relaxation time. The improvement due to the yeast appears to be comparatively independent of the physical properties of the dough. With a good quality flour such as Manitoba, the fall-off in physical properties is so slight that good bread is produced over a large range of time, while on the other hand the fall-off in physical properties is so great with a poor quality flour like English, that the best bread is produced early, and is followed by a rapid fall-off in quality.

Returning to the data in table 5, the No. 1 Manitoba had the highest initial viscosity and showed the smallest decrease in this property with time. This flour also had the highest viscosity-modulus ratio either after one or after seven hours. This is all in keeping with the general quality of the flour as shown in the bakehouse, where it behaved as by far the best of the four.

The No. 3 Manitoba, however, had a much lower initial viscosity and a much greater fall in this property with time. This low viscosity was accompanied by a low modulus, so that the initial value of the ratio of these two was high, although it fell considerably with time. This flour was not up to standard for its grade, and although it produced bread of excellent volume (low modulus) the best loaf was "thrown" relatively early, and the later loaves had much poorer "crumbs," owing to the fall in viscosity.

The Plate flour had a much higher viscosity than the No. 3 Manitoba throughout the seven hours, but this was accompanied by a rather high modulus. The ratio was lower than that for the No. 3 Manitoba at the beginning of fermentation, but decreased very little, so that at the later times the two flours approached one another in this respect. The Plate was a very good sample for its grade and gave its best bread late. The bread was of good volume, and would probably have been better if the flour had been given more water at dough making. By increasing the water content, however, the viscosity would have been lowered, so that although

the best bread would probably have had greater volume, it would have been made earlier, and might have had a poorer crumb structure.

The Australian flour with its low initial viscosity, low viscosity-modulus ratio, and considerable fall in both with time, would be expected to be much the poorest flour of the four, and this was found to be so in the bakehouse.

So far we have only dealt with doughs containing yeast. This ingredient is necessary to produce the gas which builds up dough structure, but has it any other function in bread-making?

Tests have been carried out in which the physical properties of doughs with and without yeast have been compared. The general results of these tests show that in small amounts such as are used in commercial bread-making, the effect of the yeast on the viscosity and modulus of the dough is probably not great enough to be of importance in the bakehouse. Very large amounts of yeast do affect viscosity, for example, in one case 8 per cent yeast lowered the viscosity from 3.6×10^6 to 2.9×10^6 . The effect on the modulus and on the rate of change of either property with age of the dough was, however, insignificant.

CONCLUSIONS

1. Viscosity and rigidity modulus appear to be of major importance. The viscosity must be high enough to prevent undesirable flowing-out of the dough, but on the other hand the modulus must be low, to allow big elastic expansion under the relatively low pressure of gas inside a fermenting dough. The relaxation time (which is the ratio of these two properties) is perhaps the most important single criterion of quality.

2. The water content of a dough determines the magnitude of its viscosity and modulus, and it is desirable that variations in water content should have as small an effect on these properties as possible, thus helping towards making the flour more fool-proof in the bakehouse. Whether water absorption is important in other ways, apart from financial considerations to the baker, is not known.

3. The degree to which viscosity and modulus change during the aging of the dough is of the utmost importance. The fall in viscosity with time is probably a major factor in determining the fermentation tolerance of a flour, and not only is the absolute rate of fall of this property important, but equally so is its relative rate compared with the rate of fall of modulus, since this determines the fall in relaxation time.

4. Tensile strength is a major factor in determining the extensibility and gas-holding properties of a dough, and this is of the utmost importance, since a deficiency in these properties ruins the quality of a flour even when other factors are up to standard.

5. Stickiness is important in affecting the dough's handling properties; the dough must not be too sticky to work over that range of moisture best suited to its other properties, nor should excessive stickiness develop during fermentation.

6. It is realized that such properties as work-hardening, structural viscosity, elastic hysteresis, and elastic after-effect must play their parts in determining the behavior of dough in the bakehouse, but although their significance is not yet fully understood, it is certain that they are only of secondary importance in determining the relative values of different flour samples except perhaps in certain abnormal cases.

7. It is considered that measurements of the physical properties of doughs, as far as possible in absolute units and under standard reproducible conditions, should lead to a far better appreciation of flour quality than any number of empirical tests, and should afford a sound basis for the control of quality in flour.

SUMMARY

Methods described in earlier papers for measuring the viscosity and rigidity modulus of flour doughs have been extended and developed.

The physical properties of dough are markedly affected by excessive handling, either during the preparation of the dough itself or during the preparation of the test piece. The methods used have therefore to be carefully controlled.

Viscosity and modulus measured under standard conditions of stress and strain both decrease with increasing water content or with increasing age of the dough.

Good bread-making quality is associated with a relatively high viscosity and low modulus; the relaxation time, i.e., viscosity-modulus ratio, therefore appears to be the chief single criterion of quality.

Yeast in small amounts has little effect on viscosity or modulus, and its importance in bread-making appears to be entirely due to its gas-producing activities.

Tensile strength is a major factor in determining the extensibility and gas-holding properties of a dough, but work on this property is still at too early a stage to be discussed.

Stickiness is an independent property which can be roughly measured. Its principal importance lies in its effect on the handling properties of the dough.

The investigations have proceeded far enough to show definite relations between the physical properties of flour doughs and their bread-making qualities. It is suggested that it is along these lines that further insight into the nature of flour quality will be obtained.

Our best thanks are due to Dr. E. A. Fisher, Director of the Research Association of British Flour Millers, and to Dr. R. K. Schofield of the Physics Department, Rothamsted Experimental Station, for helpful suggestions during the progress of this work.

REFERENCES

- (1) BALLU, T.: *Ann. agron.* **4**, 373 (1934).
- (2) BOUYOUCOS, G. J.: *Soil Sci.* **34**, 393 (1932).
- (3) KACHINSKI, N. A.: *Studies on the Physical Properties of Soil and on the Root-systems of Plants* (in Russian), published by Selkolkhozgiz, Moscow (1931); also *Proc. 2nd Intern. Congr. Soil Sci. Comm. I*, p. 153, Leningrad (1930).
- (4) KOSUTÁNY, T.: *Der ungarische Weizen und das ungarische Mehl*. Verlag Molnarok Lapja, Budapesth (1907).
- (5) OKHOTIN, V. V., AND SMIRNOF, O. F.: *Pedology U. S. S. R.* **2**, 237 (1934).
- (6) OSTWALD, W.: *Kolloid-Z.* **36**, 99 (1925), and many other papers.
- (7) PANKOF, A. M.: *Pedology U. S. S. R.* **1**, 80 (1934).
- (8) SCHOFIELD, R. K., AND SCOTT BLAIR, G. W.: Paper I, *Proc. Roy. Soc. London* **138A**, 707 (1932); Paper II, *ibid.* **139A**, 557 (1933); Paper III, *ibid.* **141A**, 72 (1933). See also SCHOFIELD AND SCOTT BLAIR: *Mühlenlab.* **4**, 41 (1934).
- (9) STOCK: *Z. angew. Chem.* **39**, 461 (1926), and others.
- (10) TERZAGHI, K.: *Erdbaumechnik*. Franz Deuticke, Leipzig and Vienna (1925).
- (11) WOLAROWITSCH, M. P., AND SAMARINA, K. I.: *Kolloid-Z.* **70**, 280 (1935).
- (12) ZIGLER, M. J.: *Am. J. Psych.* **34**, 73 (1923).

LIQUID AMMONIA AS A SOLVENT. V

METALLIC SOLUTIONS

JOSEPH F. CHITTUM AND HERSCHEL HUNT

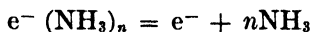
*Department of Chemistry and the Purdue Research Foundation, Purdue University,
Lafayette, Indiana*

Received December 23, 1935

This field has been ably reviewed by Johnson and Meyer (7), Johnson and Fernelius (6), Kraus (8), and Franklin (4), so that references to the literature need not be cited here. The experimental data of liquid ammonia solutions of metals is explained by a theory—namely, the dissociated metal theory—which we consider open to question. In liquid ammonia some metals, lithium, sodium, and potassium in particular, are claimed to dissociate to give a metallic cation and an electron which is solvated in dilute solutions. In more concentrated solutions even the existence of free electrons is claimed to account for the enormously low resistance of the solutions. The theory may be summarized into two equations:



where M represents Na, K, etc., and



The “solvated electron” is used to explain the anomalous conductance data, vapor pressure data, photoelectric properties, transference values, the blue color of the metallic solutions, electrolysis, and absorption spectra.

In this paper we shall report a number of experiments which directly conflict with the “dissociated metal” theory, and also give our interpretation of the data in the literature.

EXPERIMENTAL

Electrolysis

A dilute solution of ammonium chloride was electrolyzed at -60° to -80°C. , using small platinum electrodes. A blue color was detectable on the cathode surface. This blue color does not exist at the boiling point of liquid ammonia. Furthermore the evolution of hydrogen at the cathode shows that very little metallic ammonium is being formed. The small amount of blue color, however, must be due to the presence

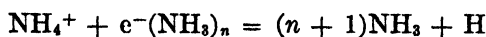
of metallic ammonium. Other data lead us to believe that the ammonium metal exists in the solution as $\text{NH}_4(\text{NH}_2^-)_2$. When a pure mercury cathode was used, with only a trace of ammonium chloride present as an electrolyte, no gas was liberated at the cathode, but there was a large amount of gas evolved at the anode. This we interpret to mean that ammonium metal is plated out and forms ammonium amalgam. A part of the cathode surface was a deep blue color during the plating process. When the amalgam was removed, it decomposed and hydrogen was liberated. NH_4 was first prepared in (l) NH_3 solutions by Moissan (9) and Rich and Travers (11). The ammonium amalgam resembles the ammonium amalgam prepared in aqueous solutions.

We then used sodium amalgam (unsaturated amalgam) as a cathode, and the only electrolyte present in the liquid ammonia was the small amount of sodium amide formed by reaction of the sodium in the amalgam with the ammonia. This solution was a very poor conductor, and it was necessary to use 220 volts across the system with the electrodes only a few centimeters apart. As soon as the current was applied blue streamers shot out from the cathode toward the anode. The speed of these particles is so high, a centimeter per second, that most of their energy must be supplied mechanically by surface tension effects and gas formation. Polarization causes the sodium and ammonium to plate out locally. The metal forms a colloidal particle and then moves away. Before reaching the anode the blue became fainter, and bubbles of hydrogen appeared which rose to the top of the liquid. There is no gas evolution at the cathode surface. In our discussion we will explain how the blue color is due to a colloid, that is, free metal with adsorbed amide ions. This negative particle is pulled away from the cathode by the applied potential. Out in the solution it becomes electrically an unstable sol. The hydrogen is produced by the decomposition of the ammonium metal, two molecules of ammonium metal giving two molecules of ammonia and one of hydrogen. According to the dissociated metal theory the blue color would be due to a solvated electron, but the decomposition of this ion could not give gaseous hydrogen. The liquid ammonia solution containing the sodium amalgam was perfectly colorless before the current was applied.

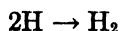
Reactions

Sodium reacted very rapidly with ammonium chloride at room temperature. At low temperature, about -70°C ., there is practically no reaction. The rate of the reaction was determined by the volume of hydrogen given off per unit of time. At room temperature, roughly 5 cc. of hydrogen was produced per minute. At the low temperature ten hours was required to produce 1 cc. The reaction rate is easy to follow qualitatively by the disappearance of the blue color. Ionic reactions should reach equilibrium

very rapidly, but a reaction with a metal with adsorption interfering would be relatively slow. The reaction



would certainly proceed very rapidly and



is known to go very rapidly with the production of much heat.

Schlubach and Ballauf explain the deficit in the hydrogen evolution by the formation of ammonium metal. They observed that only 35 per cent of the theoretical hydrogen was given off when ammonium chloride acted upon potassium solutions in liquid ammonia at -70°C . (12).

Pure mercury was added to blue, unsaturated solutions of sodium in liquid ammonia. The mercury was shaken with these solutions for several hours. The solutions were in sealed glass tubes; some of them were kept cold and some were allowed to react at room temperature. As soon as the formation of amalgam stopped, as judged by hardness and swelling, the amalgam was removed to dry tubes and the solvent ammonia allowed to evaporate. From these solid amalgams ammonia and hydrogen were liberated. When this latter decomposition took place the amalgams softened and decreased in volume.

Tyndall cone

A blue solution of sodium in liquid ammonia in a closed tube was allowed to settle carefully so that the undissolved metal and the sodium amide precipitated fell to the bottom. Dilute solutions prepared in this manner always showed a Tyndall cone.

Dialysis

Several membranes were found which were not attacked rapidly by liquid ammonia. Sodium and amide ions would diffuse through these membranes. A commercial viscose product was very satisfactory. Metallic sodium was placed in such a bag and suspended in a glass cell between platinum electrodes. Ammonia was condensed in the cell and bag. The sodium dissolved, forming a deep blue solution in the bag and some sodium amide. The amide diffused throughout the cell, but there was no blue color outside the bag. Electrodialysis was then carried out, using 220 volts. With this large potential no blue color could be pulled outside the bag. Sufficient sodium and amide ions were dialyzed to make the solution a poor conductor. This we consider as good evidence that the metal exists as a colloid.

Photoelectric properties

Kraus' experiment on the photoelectric properties of a lithium solution is confusing, since he reports a positive as well as a negative charge of the electrometer. We tested the photoelectric properties of sodium solutions in a closed cell at a low temperature, so that the ammonia vapor pressure was only 1 to 5 mm. The electrodes were of platinum and the anode was about 6 mm. above the solution. No current was detectable in a sensitive galvanometer, even when a 220-volt driving force was applied. The experiment was performed under different light intensities with the same negative result. Under the same experimental conditions pure metallic sodium showed photoelectric properties. We found that unless extreme care is used to prevent it, the ammonia will condense on the wall of the cell and thereby produce an electrical leak between the solution and the anode. Such a leak may explain the data of Kraus.

Densities of solutions

We hoped to determine the densities of solutions of alkali metals and of salts as well as of their mixtures at 25°C. However, we found that the dilute blue solutions of sodium became colorless with gas evolution when sodium bromide was added. This cannot be interpreted as common-ion effect. Surely it is due to a breaking down of the colloidal system.

If concentrated solutions of sodium were used we obtained two layers, a dense blue solution which settled to the bottom like an oil and a less dense bronze-blue layer. These latter solutions are both stable for days.

The so-called solutions of alkali metals when saturated, as at the break in the vapor pressure curve, are not homogeneous in appearance, but are sludge-like.

These data we cannot explain by the theory of Franklin and Kraus, and therefore we are offering a colloidal metal theory. The colloidal theory was first suggested by Ostwald (10). He did not propose the existence of ammonium metal in the alkali solution and therefore he tried to explain only the blue color of the solutions.

THEORETICAL INTERPRETATION OF THE DATA IN THE LITERATURE

The authors think that the alkali metals are dispersed into colloidal particles when they come in contact with liquid ammonia. They are not dispersed to atomic or ionic dimensions. At the time of peptization the metal displaces ammonium metal from the liquid ammonia according to the reaction

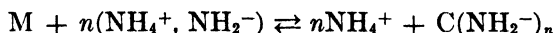


This makes the colloidal particle a colloid of an alkali metal and ammonium metal. The blue solutions can be obtained only in alkaline solution. It

is impossible to prepare ammonia so pure that it will not destroy a part of the blue color when a dilute blue solution is added to it. We do not think that the disappearance of the blue color is due to reaction with water adsorbed on the glass container. The extent to which reaction 1 takes place depends upon the activity of the two metals, the temperature, and the presence of impurities. The ion which is adsorbed in the peptizing process is the amide ion. Consequently the colloidal micelle is negatively charged. The ammonium and amide ions come from the reaction



K , the dissociation constant, of which is reported to be 10^{-33} in pure NH_3 , but the reaction rate can be increased by removing the products as they are formed. The value of K increases very little with increase in temperature, but may increase markedly in the presence of alkali metals. The alkali ions from equation 1 are removed by the amide ions that are left from reaction 2 to the extent of the solubility of sodium amide. The reaction



(where C represents colloidal metal) leaves NH_4^+ ions in the solution, that is, this reaction produces ammonium ions in solution equivalent to the colloid in solution until the electrical characteristics of the sol are such that the system is stable. The theories of metals have not been developed to the point where they would predict the appearance of a completely dispersed metal. Therefore we cannot judge the color of the solutions. On the other hand almost all colloidal solutions are colored, the color being dependent upon the particle size.

There is a point of apparent saturation of the metal in liquid ammonia. This fact can be explained using the colloidal metal theory if it is assumed that a certain definite concentration of amide ions is necessary to peptize the metal. This type of fact is known in the case of the peptization of iron in aqueous solutions of sodium hydroxide (2). The process of sol formation uses up amide ions, and when they are exhausted to a critical concentration then another type of colloid, such as the copper-colored colloid, is formed. The less active the metal the fewer amide ions required, and consequently the higher its solubility.

There is a very small change in the solubility of the metal with the change in temperature. There is obviously, therefore, very little heat of solution. This fact is very hard to explain using the metal dissociation theory. If this theory should be completely vindicated, the solution of a largely ionized substance with an infinitesimal heat of solution such as lithium in liquid ammonia would remain a remarkable phenomenon, since the solvation of the electron would give off a large amount of heat energy. The small change in the solubility with change in temperature is much more

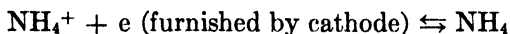
plausible in the light of the colloidal metal theory; however, little is known about the energy of peptization of metals. The heat of reaction 1 is also an unknown quantity.

There is a decrease in the vapor pressures of the solutions with increased concentration of the metal, that is fairly reproducible. Very little is known experimentally about the effect of colloids upon the vapor pressure of solvents, but theoretically the particles should serve as ions in the solution. Effectively we should have ammonium colloid in solution. If this is the case, then the vapor pressure data at least do not disprove our theory. Concentrated lithium solutions have very low vapor pressures,—much lower than Raoult's law could possibly explain. If the limiting factor is not the concentration of the lithium ion, but the adsorption of NH_3 on the metal atom as NH_4 and NH_2^- , then one does not have to postulate a large ratio of adsorbed particles per lithium atom to have a large percentage of the solvent molecules tied up. The enormous increase in activity with a slight dilution cannot possibly be due to metallic dissociation; it must be due to a decrease in the per cent of solvent adsorbed.

The molecular weight and activity of sodium have been calculated from the change in the vapor pressure with concentration of the metal. The molecular weight approaches less than 20 in dilute solutions. All of the calculations in the past have been carried out either to find out what value of molecular weight is approached at dilute solutions or to determine what the activity of the metal is, assuming Kraus' theory. The facts might be considered as some substantiation of the "dissolved and dissociated metal" theory if more were known about the extent to which salts dissolved in liquid ammonia obey Raoult's law. One of the authors (5) has carried out the determination of the activity coefficient of salts in liquid ammonia at room temperatures and has discovered marked deviations from Raoult's law. The facts about the change in the vapor pressure of the solution with change in metal concentration can be accounted for qualitatively on the basis of the formation of ammonium colloid electrolyte in solution and the marked departure from Raoult's law which would be expected in solutions of such electrolytes. The charge on the colloid particle per atom of sodium determines whether or not Raoult's law could be considered as being obeyed by these solutions. By postulating the necessary charge on the colloid (not unreasonable charges) the data could be accounted for assuming Raoult's law.

The disappearance of the blue color around the anode when a dilute metallic solution is electrolyzed we explained by the oxidation of NH_4 to NH_4^+ , which immediately reverses equilibrium 2 with an increase of NH_3 or solvent in the anode compartment. Amide ions are plentiful, since they were adsorbed on the colloidal metal. This, of course, removes the source of the blue color, and since the ions are removed the solution immediately

around the anode will become a very poor conductor. Furthermore, at the same time NH_4^+ is removed from the anode by attraction to the cathode. This explains the absence of visible products of electrolysis at the anode. The NH_4^+ will be an excellent carrier of electricity in its parent solvent (1). The cathode compartment will become richer in the blue color because



and secondly because of transference of the existing blue particle. The ionic atmosphere of the fast moving ammonium ion will contain the colloidal negative particle $\text{C}(\text{NH}_2^-)_x$. If the sodium or potassium ion is present it will also act as a positive carrier. These ions are not liberated, however, since this would require a greater potential. By our theory or the accepted theory, the free metal simply would ionize again. Reaction 1 will go to completion only at the anode. If the concentration of the solution is increased the conduction should become more and more metallic, owing to the increase in concentration of the colloidal particles. This will also shift the fraction of the current carried by the positive and negative carriers. The NH_4^+ will carry most of the current in the dilute solutions, since the larger colloid particle is less mobile, but when the concentration reaches a certain limit, the mobility of the negative carrier will no longer be an important factor, as the conduction is by electronic transfer (3). As a higher metal concentration is reached one would expect the ionic concentration to decrease and consequently the apparent molecular conductance. The two will not necessarily counterbalance, and we should expect a minimum conductance. This minimum has been reported by all investigators in the neighborhood of 0.05 normal. Our theory would predict a higher conductance than for a similar concentration of a salt because of the nature of the conductors.

The specific conductance of mercury is approximately two and six times, respectively, the specific conductance of a saturated and a 2 *N* solution of sodium. Preliminary experiments in this laboratory showed that the resistance offered a d.c. current by a sodium solution is decreased roughly 50 per cent by the addition of sodium chloride. This must be explained by an orientation of the conductors into a complicated "bridge-work" which favors electronic conduction. The addition of a common ion should decrease the concentration of the free electron, and therefore greatly increase the resistance of the solution.

There is a large positive temperature coefficient of the electrical conductivity that does not decrease in value with increasing temperature. This fact cannot be explained using the dissociated metal theory. Ordinary electrolytes have their conductivities pass through a maximum. Metals have negative coefficients. The increasingly large positive tem-

perature coefficient is just what the colloidal metal theory would predict. There would be an increasing number of collisions between metal particles, and consequently an increasing percentage of metallic conductivity with the increase in temperature.

The absorption spectra of the alkali metal solutions are the same. This interesting fact can be interpreted as indicating that the colored component of all these dilute solutions is the solvated electron. The colloidal metal theory postulates that the metal colloid, especially in the dilute sol, is largely ammonium metal with a core of alkali metal. In the formation of a dilute colloidal solution the procedure is quite uniform. Since the composition of the outer part of the colloidal particles (no matter what alkali metal is dispersed) is the same, since the methods of formation of the various colloids are the same, and since all of the colloids are quite stable, it follows from the principle of Hevesy that the rotational-vibrational-electron-transition spectra should be quite similar for the sols of the various alkali metals.

The densities of the solutions of the alkali metals in liquid ammonia pass through a maximum density with increasing concentration of the metal. The change in density of these solutions is credited to the existence of electrons associated with ammonia molecules. It seems to the authors that this explanation is especially weak, since metals are in general very dense and the more dense the metal, the greater the possibility of having more free electrons per atom. It is well known that colloids greatly change the internal energy of liquids under most circumstances. Colloids lower the surface tension of a liquid; thereby they decrease the force compressing a liquid, and the density would be decreased. The charged forces in the colloidal solution will increase the free space between particles, so that the density will be decreased. The density of the free ammonium metal is an unknown factor, but we predict that it is less than 0.5 g. per cubic centimeter and that it will therefore decrease the density of the solution. The relative amount of free ammonium metal will change with the concentration of the dissolved metal as well as the closeness of packing of the adsorbed particles, so that the magnitude of the final density cannot be estimated. The closeness of packing should be greater for potassium than for sodium; therefore, one would predict a smaller increase in volume for potassium than for sodium solutions. This prediction agrees with the experimental data. The metallic ionic radii of sodium and potassium are of the wrong relative order to explain it, and the "solvated electron" should have the same density in both solutions.

Metals such as platinum will catalyze the decomposition of NH_4 through the removal of H_2 .



Therefore the rate of formation of sodium amide from liquid ammonia and metallic sodium will be increased. If the metal furnishes a colloidal metal surface under the experimental conditions, it will be a better catalyst for the reaction.

SUMMARY

1. Methods for producing ammonium metal in liquid ammonia have been described. Its presence in alkali metal solutions has been proven.

2. The "dissociated metal" theory of metallic ammonia solutions is critically discussed, and a colloidal metal theory is outlined to explain the properties of these solutions.

3. The alkali solutions are evidently mixtures, and therefore the physical data are not capable of interpretation on the basis of the well-known laws of physical chemistry.

REFERENCES

- (1) BERNAL AND FOWLER: *J. Chem. Physics* **1**, 515 (1933).
- (2) CHITTUM AND RITCHEY: Unpublished work.
- (3) FARKAS, L.: *Z. physik. Chem.* **161A**, 355 (1932).
- (4) FRANKLIN, E. C.: *The Nitrogen System of Compounds*, American Chemical Society Monograph. The Reinhold Publishing Corporation, New York (1935).
- (5) HUNT AND LARSEN: *J. Phys. Chem.* **38**, 801 (1934); **39**, 877 (1935).
- (6) JOHNSON AND FERNELIUS: *J. Chem. Education* **6**, 20 (1929).
- (7) JOHNSON AND MEYER: *Chem. Rev.* **8**, 273 (1931).
- (8) KRAUS, C. A.: *Properties of Electrically Conducting Systems*, American Chemical Society Monograph. The Reinhold Publishing Corporation, New York (1922).
- (9) MOISSAN: *Compt. rend.* **144**, 790 (1907); **133**, 803 (1901).
- (10) OSTWALD, WOLFGANG: *Kolloidchem. Beihefte* **2**, 437 (1910-11).
- (11) RICH AND TRAVERS: *Proc. Chem. Soc.* **22**, 136 (1906); *Trans. Chem. Soc.* **69**, 872 (1906).
- (12) SCHLUBACH AND BALLAUF: *Ber.* **54B**, 2825 (1921).

THE FLOCCULATION OF THE STANNIC OXIDE SOLS

H. S. VAN KLOOSTER AND A. PETROVICH

Department of Chemistry, Rensselaer Polytechnic Institute, Troy, N. Y.

Received November 21, 1935

INTRODUCTION

The character of the stannic oxide sols was first studied methodically in the laboratory of Zsigmondy, where Franz (1) compared the peptizing ability of potassium and sodium hydroxides for the so-called alpha and beta stannic oxides. Varying amounts of alkali were used to give sols with stannic oxide:alkali ratios of 2, 10, 25, 50, and 100. It was found that potassium hydroxide was definitely better than sodium hydroxide, and that the β -oxide gels were more difficult to peptize than the α -oxide gels.

Heinz (2) investigated the flocculation of the sols from freshly precipitated or α -stannic oxide by certain salts whose action was found to be divided into two groups. Salts such as sodium chloride, sodium nitrate, sodium sulfate, and sodium acid sulfate produced flocculation at greater concentrations than those of the type of calcium chloride, barium chloride, aluminum chloride, and silver nitrate, the concentrations of the latter group in each case being the same as that of the peptizing alkali for the standard 10-cc. samples. Also, upon the addition of water the first group was reversible while the second was not. These values are summarized by Krzyt (van Klooster) (3).

From these experiments, Zsigmondy (8) assumed that peptization of stannic oxide by alkali formed particles of hydrous stannic oxide with stannate ions adsorbed to give the double layer. Discharge of the double layer was accomplished by the first group of electrolytes, whereas the second group produced insoluble stannates and destroyed the double layer to produce precipitation.

Varga (5) and Wintgen and coworkers (7) investigated the conductivity and transport of the sols to obtain an idea of the structure of the micelle expressed as the number of SnO_2 atoms associated with K_2O . It was shown that for sols with a SnO_2 :KOH ratio of 50, about 15 per cent of the potassium stannate molecules occurred in the mobile part of the double layer, while 85 per cent were outside.

This work was undertaken to prepare similar sols, using ammonium hydroxide and lithium hydroxide as peptizing agents for the α -stannic oxide gel in addition to potassium hydroxide and sodium hydroxide, and

to determine flocculation values for salts of potassium, ammonium, lithium, and sodium. It has been shown that the α - and β -forms of the stannic oxide are not allotropic forms but have the same crystal structure; the terms so used mean freshly formed and aged products, respectively (6).

EXPERIMENTAL

In the preparation of potassium hydroxide, Küster's (4) method was used. Water vapor acted slowly upon metallic potassium to give a 40 per cent alkali solution, which was diluted to about 1 normal and standardized.

The sodium hydroxide solution was made up to about 17 normal, when the carbonate was precipitated, and after decantation and filtration was diluted to 1 normal. Lithium hydroxide was prepared in like fashion.

The electrolytes used for flocculation were of analytical purity and were made up to exactly 1 normal.

The stannic acid gel was prepared after Zsigmondy and Heinz (2). 7.300 g. of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (Eimer and Amend) was dissolved in about 1 l. of doubly distilled water and allowed to remain in a dark place at room temperature for a period of three days, until the white gelatinous precipitate had settled. The supernatant liquid was siphoned off and more water was poured in its place. The oxide was washed repeatedly until the off-coming liquid gave no test for chloride and the conductivity reached 4×10^{-6} mhos. The last washings were made with distilled water having a conductivity of 1.0×10^{-6} . In all, fifteen to twenty washings were required.

The gel was transferred gradually to a 250-cc. volumetric flask, allowing the water to separate until the volume of gelatinous oxide was approximately 235 cc. It was found that if the total volume of gel was below 220 cc., difficulty in peptization was experienced, particularly in sols with SnO_2 :KOH ratios of 25, 50, and 100.

The calculated amount of alkali necessary for peptization was pipetted into the flask, the volume made up to exactly 250 cc., and the flask shaken vigorously until the peptization was complete. Finally, the solutions were transferred to Pyrex flasks and tightly closed with stoppers coated with tin foil.

In the sols of ratio 50 and 100, heat had to be applied. Sols of ratio 50 required heating for at least an hour, while those of ratio 100 required heating for five hours on a water bath. The sols of ratio 100 for lithium hydroxide could not be prepared, and for sodium hydroxide the stability was less than twenty-four hours. Likewise the ammonium hydroxide sol of the same ratio was not any more stable than that of sodium hydroxide.

The sols of ratio 2 were clear and without color, except in the case of lithium hydroxide where a decided blue was evident, reminiscent of the

appearance of dilute mastic sols. The colloids with stannic oxide:alkali ratio of 10 were transparent but possessed a slight tinge of blue, noticeably more intense in the ammonium hydroxide sol. The Tyndall effect was more evident in the sols of ratio 25, while the sols in which the ratio of stannic oxide to alkali was 50 and 100 were opalescent and opaque, respectively. The sols of ratio 2 and 10 were basic in reaction, showing the presence of free alkali; in the ammonium hydroxide sol of ratio 2, an odor of ammonia was present.

Sols of ratios 2, 10, and 25 were stable after remaining in a cupboard for more than a year without any outward change, except that the $\text{SnO}_2\text{-NH}_4\text{OH}$ sol of ratio 2 became opalescent. Sols of ratio 50 for ammonium hydroxide and lithium hydroxide and all of ratio 100 were found, after four months, to have settled into an opaque layer, below a transparent layer. On shaking, these sols became apparently homogeneous, but after some time again separated into layers.

In performing the flocculation experiments, a certain technique was always employed. The sols were chosen so that two weeks had elapsed since the beginning of hydrolysis to the gel form, with the exception of the sols of ratio 100, which were used as soon as peptized.

The peptized sols were pipetted into Pyrex test tubes of dimensions 16 x 150 mm. The initial concentrations of stannic oxide in the sols were adjusted so that 8 cc. of sol contained 0.666 milliequivalent of stannic oxide, while the alkali used for peptization was such as to give the proper ratios.

Eight cubic centimeters of the sol was pipetted into a Pyrex test tube previously steamed. The precipitating electrolyte in varying amounts was added to the test tubes and the total volume made up to 10 cc. in each case. The tubes were closed with tin foil-covered stoppers, inverted ten times, and set in a rack. After exactly 1 hour the tubes were inspected for flocculation. The procedure was carried out at approximately $25^\circ\text{C}.$, and the colloids were shielded from sunlight throughout. A sol was considered as flocculated when a clear ring was seen below the whole of the meniscus, separating the opaque gel.

Usually series of experiments were run with the interval between quantities of added electrolyte made less until the accuracy was in the vicinity of 5 per cent. In sols of higher ratios, the accuracy was somewhat below 10 per cent.

Alcohol numbers were determined with 5 cc. of sol as standard. A quantity of alcohol (purified with silver oxide) that would cause precipitation in 1 hour was the alcohol number. This precipitation was reversible, as were those with the electrolytes.

Experiments were carried out on the flocculation by electrolytes of alcohol-containing sols. A total volume of 15 cc. was used, excepting in sols

of ratio 2. Five cubic centimeters of alcohol were added to 8 cc. of sol in the test tube, and the remainder made up with electrolyte and water. The procedure was otherwise identical with the flocculations with electrolytes.

RESULTS

The results are shown in tables 1 to 4.

TABLE 1

Flocculation value of stannic oxide-potassium hydroxide sols
Milliequivalents per 10 cc. (total volume)

SALT	SnO ₂ : KOH RATIO				
	2	10	25	50	100
NaCl.....	1.8	0.85	0.145	0.070	0.085
NaNO ₃	1.9	0.80	0.140	0.070	0.085
Na ₂ SO ₄	2.2	0.75	0.155	0.075	0.085
KCl.....	>10	0.85	0.155	0.080	0.090
KNO ₃	>10	0.90	0.160	0.075	0.090
LiCl.....	0.48	0.30	0.105	0.075	0.080
Li ₂ SO ₄	0.50	0.32	0.105	0.070	0.085
NH ₄ Cl.....	1.5	0.44	0.155	0.065	0.080
Alkali per 10 cc.....	0.333	0.066	0.0266	0.0133	0.0065
C ₂ H ₅ OH (in cc.) to 5 cc. of sol.....	3.08	>500	>500	>500	

TABLE 2

Flocculation values of stannic oxide sols
Milliequivalents per 10 cc. (total volume)

SALT	SnO ₂ : ALKALI RATIO					
	SnO ₂ -NaOH sols		SnO ₂ -LiOH sols		SnO ₂ -NH ₄ OH sols	
	2	10	2	10	2	10
NaCl.....	1.7	0.75	0.85	0.60	1.7	0.65
NaNO ₃	1.8	0.70	0.85	0.45	1.15	0.60
Na ₂ SO ₄	2.0	0.65	1.20	0.85	>10	0.65
KCl.....	>10	0.70	>10	0.80	>10	0.80
KNO ₃	>10	0.80	>10	0.80	>10	0.75
LiCl.....	0.43	0.30	0.30	0.28	0.52	0.31
Li ₂ SO ₄	0.42	0.30	0.35	0.30	0.56	0.31
NH ₄ Cl.....	1.40	0.40	0.80	0.88	1.5	0.40
Alkali per 10 cc.....	0.333	0.066	0.333	0.066	0.333	0.066
Alcohol number.....	1.36	>500	1.70	>500	>250	>500

TABLE 3

Flocculation values of stannic oxide-potassium hydroxide-alcohol sols
 Milliequivalents per 15 cc.

SALT	SnO ₂ KOH RATIO			
	2	10	25	50
	4 cc. C ₂ H ₅ OH added	5 cc. C ₂ H ₅ OH added	5 cc. C ₂ H ₅ OH added	5 cc. C ₂ H ₅ OH added
NaCl.....	0.13	0.135	0.055	0.009
KCl.....	0.10	0.160	0.065	0.009
LiCl.....	0.12	0.110	0.060	0.008
NH ₄ Cl.....	0.52	0.125	0.070	0.009
NaNO ₃	0.090	0.105	0.070	0.007

TABLE 4

Flocculation values of stannic oxide-alkali-alcohol sols
 Milliequivalents per 15 cc.

SALT	SnO ₂ . ALKALI RATIO					
	SnO ₂ -NaOH sols		SnO ₂ -LiOH sols		SnO ₂ -NH ₄ OH sols	
	2	10	2	10	2	10
NaCl.....	Flocculated	0.12	Flocculated	0.100	0.140	0.125
KCl.....	by	0.14	by	0.125	0.190	0.135
LiCl.....	C ₂ H ₅ OH	0.10	C ₂ H ₅ OH	0.100	0.140	0.125
NH ₄ Cl.....		0.12		0.110	0.155	0.160
NaNO ₃		0.15		0.110	0.140	0.120
C ₂ H ₅ OH.....	2	5	2	5	5	5

DISCUSSION

From the results of peptization, it is seen that potassium hydroxide produces the sols most easily, whereas lithium hydroxide gives the greatest difficulty. Sodium hydroxide and ammonium hydroxide rank in between, in the order named. The order is evident if the time for conversion of the opaque gel of the hydrous oxide to the sol is compared qualitatively, and then it is seen that potassium hydroxide produces a clear sol by mixing thoroughly for a few seconds, sodium hydroxide taking a longer time, while ammonium hydroxide requires several minutes. The stannic oxide-lithium hydroxide sol of ratio 2 has not been obtained without the bluish appearance that is characteristic of the usual sols of ratio 50. Likewise it is seen in the sols of stannic oxide:alkali ratio equal to 100, that the potassium hydroxide sol is relatively stable, while the lithium hydroxide sol could not be prepared at all.

From the flocculation experiments, it is seen that the cations may be

arranged in the order of decreasing flocculation values: $K > Na > NH_4 > Li$. The order is most evident in sols with a stannic oxide:alkali ratio of 2 and 10, less so for 25, and not at all for 50 and 100, where flocculation values are approximately the same for a single sol and for different sols of like ratio. This order however, is the reverse of the lyotropic series for hydrophobic sols such as Oden's sulfur and arsenic trisulfide sols and for the molybdenum pentoxide and vanadium pentoxide sols (3), but agrees with the usual series for emulsoids and is thus interpreted as a salting-out effect, so that hydration is a factor for consideration.

It is known that lithium has the greatest amount of water attached to the ion, while potassium has the least. Also it is indicated that the stannic oxide colloid is composed of particles of hydrous SnO_2 and has hydrophilic properties.

In considering the mechanism of peptization, the alkali has the effect of breaking up the gel into small particles of SnO_2 , with the adsorbed stannate formed by chemical reaction giving rise to the double layer. As more alkali is introduced, the particles are expected to be smaller and the opacity of the gel to decrease with the greater dispersion. It is seen, however, that the ion with the greatest amount of water associated with it peptizes the stannic oxide gel with the greatest difficulty and conversely, so that the water of the ion may be viewed as a hindrance. From the experiments of Zsigmondy and Glaxelli (9), it is found that compressing the micelles as in ultrafiltration or even ordinary filtration increases the amount of alkali needed for peptization, probably owing to the removal of some water from the gel, and this process may be responsible for the aging of the α -oxide into the β -form.

In the flocculation experiments, it is noted that the ion with the greatest amount of water coagulates the sol with the greatest ease. Possibly an equilibrium of the water carried with the ion has to be considered. By lowering the hydration, the stability factor induced in hydrophilic colloids is reduced so that smaller amounts of cation will be needed to discharge the double layer to cause coagulation. If an ion that tends to dehydrate a particle be used for peptization, smaller flocculation values for these sols are expected as compared with sols of an alkali ion with a smaller water mantle. This seems to be borne out by the sols prepared from lithium hydroxide.

The flocculation values for the sols from potassium hydroxide are not in numerical agreement with the values of Heinz (2) because of a difference in technique.

The alcohol numbers show that sols of ratio 2 are coagulated while the others are not. Since the stannates are only slightly soluble in ethyl alcohol, it may be that the alkali stannate has its solubility reduced so as to cause flocculation, which is reversed with the addition of more water.

It is seen that the addition of alcohol lowers the amount of electrolyte needed to bring about coagulation. The lyotropic series is evident in the presence of alcohol, but the flocculation values are smaller. The values of table 3 express this clearly. Table 4 shows a decrease for the sols prepared with sodium hydroxide and lithium hydroxide, except that for these two sols no values were obtained for the ratio 2 because of coagulation by the alcohol alone. Stannic oxide-ammonium hydroxide sols are less sensitive to alcohol. Alcohol may be said to possess two actions,—one of reducing the solubility of the adsorbed stannate, the other a dehydrating action.

SUMMARY

Stannic oxide sols were made with lithium hydroxide and ammonium hydroxide so that the ratios of stannic oxide to base varied from 2 to 50, together with those peptized by potassium hydroxide and sodium hydroxide, previously studied by Heinz (2).

Flocculation values were determined with salts of potassium, sodium, lithium, and ammonium, and also for the same sols containing alcohol.

REFERENCES

- (1) FRANZ, R.: Beiträge zur Chemie der Zinnsäuren vom Kolloidchemischen Standpunkt aus. Dissertation, Göttingen, 1913.
- (2) HEINZ, E.: Über Kolloide Zinnsäuren wechselnden Alkaligehaltes. Dissertation, Göttingen, 1914.
- (3) KRUYT, H. R.: Colloids, translated by H. S. van Klooster. John Wiley and Sons, New York (1930).
- (4) KÜSTER: Z. anorg. Chem. **13**, 134 (1897); **41**, 474 (1904).
- (5) VARGA: Kolloidchem. Beihefte **11**, 1 (1919).
- (6) WEISER: Inorganic Colloid Chemistry, Vol. II, p. 233 ff. John Wiley and Sons, New York (1935).
- (7) WINTGEN ET AL.: Z. physik. Chem. **103**, 238 (1922).
- (8) ZSIGMONDY: Kolloidchemie, 3rd edition, or Chemistry of Colloids (translated by Spear), p. 152 ff. John Wiley and Sons, New York (1917).
- (9) ZSIGMONDY AND GLIXELLI: see Kolloidchemie, 3rd edition, p. 245.

LIESEGANG RINGS OF MANGANESE SULFIDE. II

OLIN F. TOWER

Morley Chemical Laboratory, Western Reserve University, Cleveland, Ohio

Received November 21, 1935

Some years ago Chatterji and Dhar (1) published an account of a number of experiments on the formation of Liesegang rings in many gelatinous media, among them silica gel. They reported that they obtained rings of cadmium and antimony sulfides in this gel. However, they gave no detailed directions as to concentrations and other conditions under which the rings formed.

For some years we have been interested in the formation of bands of metallic sulfides in gels, and have recently tried to form bands of such sulfides in silica gel. The experiments were not altogether successful, as only faint rings were obtained, and these under varying conditions which could not always be reproduced. The rings so formed were those of zinc, cadmium, and antimony sulfides. As we had obtained excellent bands of manganese sulfide in gelatin (4), we tried to form rings of this substance in silica gel. We found the best procedure to be the following: Commercial water glass was diluted to a density of 1.07 and was mixed with an equal volume of 0.5 N acetic acid. This mixture, which reacted acid toward litmus, was poured into test tubes 1 in. in diameter until they were three-fourths full, and then the whole was saturated with hydrogen sulfide gas. The tubes were then allowed to stand until the contents set to a gel, after which the upper portion of the tube was filled with a solution of manganese chloride. The concentrations of manganese chloride giving the best bands were from 0.5 to 1 molar. The bands obtained are shown in figure 1. The rings usually obtained were like figure 1 a and b, but occasionally rings of the type shown in figure 1 c were produced. As far as the concentration of the manganese chloride is concerned, there seemed to be no difference whether the fine banded or coarsely banded ones were obtained, so the cause of this difference must have lain in the nature of the silica gel or in the concentration of the sulfide ion in it, as it is obvious from the method of preparation that the latter could not be accurately controlled. Attempts to control the concentration of the sulfide ion by using definite concentrations of sodium sulfide were unavailing, as this rendered the medium alkaline and the mixture failed to gel.

APPLICATION OF HUGHES' DIFFUSION THEORY

E. B. Hughes (3) has recently developed a theory of the formation of Liesegang rings, based on diffusion. The theory is essentially in accord with that originally advanced by Wo. Ostwald, but Hughes has worked out mathematically the conditions for the formation of a new band on the basis of the upper electrolyte diffusing in and building up a sufficient concentration to attain the solubility product of the insoluble substance anew. In order to apply the equations it is necessary to determine the distance between bands and the time of the formation of each band.

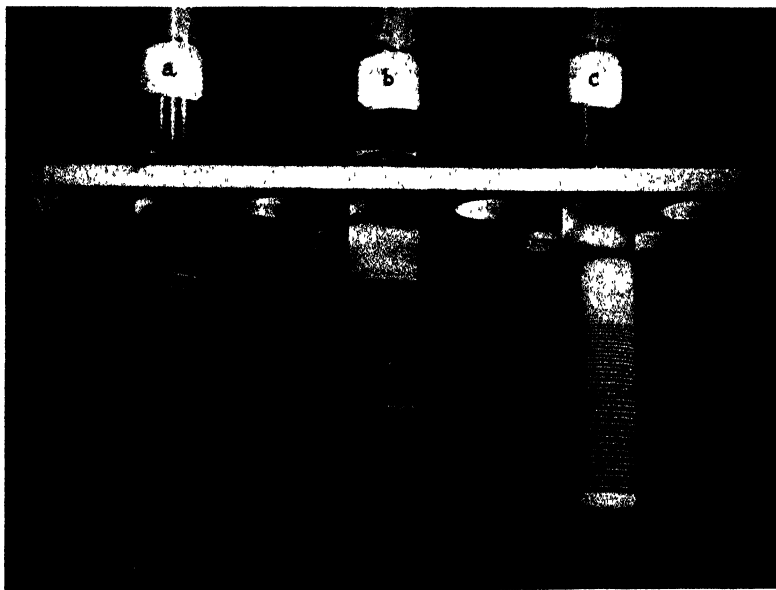


FIG. 1. Liesegang rings of manganese sulfide in silica gel

As bands of manganese sulfide could be reproduced very readily in gelatin, bands of this material and in this gel were used to test the theory. As seen in figure 1 a and b, a heavy precipitate of manganese sulfide was always produced at the junction of the two electrolytes. The thickness of this precipitated area varied greatly in different cases, and in general was greater the greater the difference in concentration of the Mn^{++} ion above from that of the S^{-} ion in the gel. The thicker this precipitated band, the more slowly the Mn^{++} ion diffused through it and the longer was the initial period before the first Liesegang ring formed. Another difficulty in measuring the time of formation of the bands was the long time consumed in completing the formation of the rings, viz., ten to twenty days. Naturally, therefore, some of the rings would form in the middle of the

night, and the time of their formation would not be exactly fixed. However, since the time between the formation of successive rings was long, this error was small. On account of the varying thickness of the initial banded precipitate, the time was measured from the end of the formation of this band. The appearance of the rings in gelatin can be observed in figure 1 of the former article (5). The results obtained from two such experiments are given in table 1. In the first column are the distances of each ring from the point of beginning, and in the second column the time of the beginning of the formation of each band. h_n/h_{n-1} represents the distance of each band divided by the distance of the preceding band. h/\sqrt{t} represents the distance of each ring divided by the square root of the time of its formation.

TABLE 1
Measurements made on rings of manganese sulfide

1 M MnCl ₂ ; 0.15 M (NH ₄) ₂ S				0.25 M MnCl ₂ ; 0.15 M (NH ₄) ₂ S			
h in cm.	Time in hours	$\frac{h_n}{h_{n-1}}$	$\frac{h}{\sqrt{t}}$	h in cm.	Time in hours	$\frac{h_n}{h_{n-1}}$	$\frac{h}{\sqrt{t}}$
1.45	14		0.3875	1.06	11		0.3915
1.85	24	1.276	0.3776	1.35	18	1.276	0.3182
2.35	38	1.270	0.3812	1.72	27.5	1.274	0.3280
2.95	54	1.255	0.4014	2.20	39	1.279	0.3523
3.70	82	1.254	0.4084	2.75	62	1.250	0.3492
4.45	116	1.203	0.4132	3.40	90	1.236	0.3584
5.25	162	1.180	0.4125	4.15	128	1.220	0.3668
6.20	217	1.181	0.4209	5.00	193	1.205	0.3599
7.35	280	1.184	0.4393	6.00	269	1.200	0.3659
8.80	400	1.197	0.4400	7.25	391	1.208	0.3667
Thickness of initial precipitate, 3 cm.				Thickness of initial precipitate, 1.9 cm.			

According to Hughes' theory the numbers in the last two columns should be constant. This is seen to be the case approximately. The numbers in the third column being approximately constant show that the rings are in geometrical progression, which has been found to be the case in most experiments of this kind. Many determinations of these values were made in other experiments, and the average found for rings of manganese sulfide of varying distances apart was 1.21.

Hughes has derived an equation¹ giving the value of this constant in

¹ Equation (ii), Kolloid-Z. **72**, 213 (1935). To illustrate his theory he uses the results obtained by Morse and Pierce (Z. physik. Chem. **45**, 589 (1903)) with bands of silver chromate in gelatin. These bands were all complete in from one to one and three-quarters hours after the beginning of the experiment, and consequently results are to be expected differing considerably from those described here, where the time taken for the formation of a series was from ten to twenty days.

an independent manner, which requires for its solution the value of the solubility product of the substance forming the bands. The solubility product of manganese sulfide in water is 1.4×10^{-15} . Its solubility product in gelatin would have to be about 3.6×10^{-3} in order that Hughes' equation ii should have a value for K equal to 1.21. This of course is highly improbable. However, from the appearance of the bands when they begin to form, it is evident that the solution is highly supersaturated, for a band appears rapidly in voluminous quantity and then gradually increases in density and thickness. This seems to show that the sulfide ions build up a concentration considerably in excess of that required for the solubility product of manganese sulfide before a band begins to form. Furthermore, the strong adsorption of manganese² ions by the bands previously formed (2) delays the formation of a new band. For these reasons it is somewhat remarkable that the numbers in the fourth column in the table are as constant as they are.

SUMMARY

1. A method for obtaining Liesegang rings in silica gel is described.
2. Manganese sulfide bands in silica and other gels are spaced approximately in geometrical progression, the multiplier having the average value of 1.21.
3. Although in general the bands of manganese sulfide are formed by a process of diffusion essentially in accord with Hughes' theory, the time of formation of the bands is considerably influenced by supersaturation and adsorption.

REFERENCES

- (1) CHATTERJI AND DHAR: *Kolloid-Z.* **40**, 97 (1926).
- (2) DAUS AND TOWER: *J. Phys. Chem.* **33**, 608 (1929).
- (3) HUGHES: *Biochem. J.* **28**, 1036 (1934); see also *Kolloid-Z.* **71**, 100 (1935).
- (4) TOWER AND CHAPMAN: *J. Phys. Chem.* **35**, 1474 (1931).
- (5) Reference 4, p. 1475.

* Analysis of the manganese sulfide precipitate, which composes the rings, shows an excess of manganese over sulfur of 25 per cent above that required for the formula MnS .

ACTIVATION OF REDWOOD AND ASH-FREE SUGAR CHARCOAL IN A CURRENT OF AIR

JAMES W. McBAIN AND R. F. SESSIONS

Department of Chemistry, Stanford University, California

Received January 30, 1936

It is difficult to ascertain from the literature¹ exactly what are the optimum conditions for the air activation of charcoal, or exactly what happens during the processes of activation. Attempts at activation in a current of air are easily frustrated by a lack of attention to detail or to conditions in different parts of the mass of the charcoal. Similarly, so numerous are the factors involved that occasionally an exceptional success is achieved which it may prove impossible to duplicate.

The present studies have been carried out over a series of many years, first with charcoal derived from redwood (*Sequoia Sempervirens*), as studied by Dr. F. Carlyle Harmon, and then by one of us (R.F.S.) with sugar charcoal, which is practically the only source of highly active, ash-free charcoal.

It early appeared that these results differed from the finding of Lamb, Wilson, and Chaney and their associates (6) that the optimum temperature for air activation lies between 350° and 450°C. We find indeed that there is a peak of activation at this temperature, but also find that an even more pronounced peak with still better activation occurs between 920° and 960°C. Above this, usually the activity of charcoal falls off very rapidly. However, the very best sugar charcoal ever obtained was that made by H. Greville Smith (8) in the chemistry department at Bristol University. He prepared a large sample by heating Kahlbaum sugar charcoal in a slow current of air at 1130°C., with an intermission required for repairing the horizontal Hereaus tube platinum resistance furnace. Its activity (81 per cent) equalled that of good activated wood or commercial charcoal. We find that the activity of charcoal activated at a particular temperature may be improved or impaired by subsequently submitting it to another temperature. Generally it is much improved by reactivating with air at the same temperature after an intermediate cooling to room temperature with exposure to air.

¹ For a recent résumé of the patent literature see reference 5. For modern conceptions of the nature of activated charcoal, see references 5 and 1.

EXPERIMENTAL

Preparation of redwood charcoal

The redwood charcoal used for these determinations was made by carbonizing redwood strips 4 cm. wide and 0.7 cm. thick in an atmosphere of nitrogen at very low pressure at 450°C. The carbonized strips were crushed and only the pieces passing a 6-mesh but retained by a 10-mesh screen were used for activation. The original activity of this charcoal was 15.1 per cent, as determined by the percentage of iodine removed from 50 cc. of 0.2 *N* solution by 1 g. of 200-mesh carbon in 3 minutes.² The slow distillation of dry redwood yields a harder charcoal than the rapid distillation of wet material. Sapwood produced the hardest and light wood the softest charcoal. Carbon tetrachloride tests of activated redwood charcoal, whether from heartwood or bark, indicated that although highly satisfactory for sorption from solution, it has but little retentive value for gases, being only somewhat better than bone char.

Preparation of sugar charcoal

Five different grades of sugar charcoal were used in these experiments. These will be referred to henceforth as Nos. 1, 2, 3, 4, and 5.

Charcoals No. 1 and 2 were prepared from Baker's sucrose ("c.p. analyzed crystals"). Five pounds of sucrose were carbonized in an 18-quart aluminum kettle, the highest temperature attained being about 200°C. The charred mass was then removed to an aluminum pan, placed in an electric furnace, and the temperature raised to 400°C., being at 360° to 400°C. for 30 minutes. At the end of this period, the charcoal was cooled in air, ground to 20-mesh, washed three times in warm distilled water, drained, and dried for 15 hours at 105°C.

The first portion of this charcoal (No. 1) was not covered immediately upon removal from the furnace, and as a result there occurred a glowing of the charcoal that probably caused the temperature to go much above 400°C. The activity of this charcoal was 27.02 per cent before washing and 21.57 per cent after washing. The second portion (No. 2) was covered immediately upon removal from the furnace and then allowed to cool. Its activity was 3.53 per cent before washing and 8.84 per cent after, both activities being determined by the iodine method.²

Sugar charcoal No. 3 was also Baker's sucrose ("c.p. crystals"). It was caramelized or possibly carbonized in an aluminum kettle at 200°C., and

² Standard method of determining "activity" (Chaney, N. K., Ray, A. B., and St. John, A.: *Ind. Eng. Chem.* **15**, 1248 (1923)). However, we have found that the results have a high temperature coefficient; thus, an "activity" determined as 7 per cent at 4°C. becomes 15.5 per cent at 25°C. and 27 per cent at 65°C. We have therefore measured at 20°C.

removed to porcelain crucibles; the latter were covered to keep out as much air as possible, and then placed in a muffle furnace and heated to 900°C. for 15 minutes. Upon removal from the furnace, sample No. 3 was chilled rapidly and stored in glass bottles. Its activity before being heated to 900°C. was 14.5 per cent, and after heating was 20.25 per cent. The ash content of these three sugar charcoals was less than 0.00 per cent.

Sample No. 4 was Kahlbaum's "charcoal from sugar" with an original activity of 14.5 per cent. Its temperature of formation is unknown. Its ash content was 0.12 per cent.

Sample No. 5 was prepared by C. I. Glassbrook by dropping pure sugar through crossed electric arcs operating at 400 volts and 6 amperes and at 100 volts and 26 amperes, respectively. After washing, it was a spongy, wet, black mass, with an activity of 14.7 per cent. After drying at 105°C., this fell to 5.8 and 6.4 per cent. Upon air activation at 920°C., two different specimens showed activities of 30 per cent and 20 per cent, respectively.

ACTIVATION OF REDWOOD CHARCOAL

The activities of the redwood charcoal after heating in an iron retort for 6 hours at a fixed temperature in a current of air at low pressure are shown in table 1 and figure 1. The results in this table indicate two maxima, one at about 368°C. and the other at 800°C. with a marked minimum between. Dr. Harmon suggested that the lower maximum might be due to combustion to carbon dioxide and the second to carbon monoxide. It appears more likely that these two peaks are connected with the fact that at these two temperatures different types (3, 12) of active charcoal are formed, both as regards sorption of alkali and as regards the order of the Traube series.

These results were repeated by H. W. Hobbie and then again by one of us (R.F.S.) to a substantially similar effect, with the additional information that very little difference was observed when the air was at 14 mm. or at atmospheric pressure. Furthermore, when redwood charcoal which had already been activated at temperatures between 370° and 770°C. and cooled in air, was heated in an atmosphere of nitrogen or helium, the activity was still further increased. A sample air-activated at 770°C. with a value of 33 per cent, upon heating to 920°C. in nitrogen showed a final activity of 64 per cent. Even charcoal which has not been activated but merely exposed to air at room temperature becomes moderately activated upon heating to 800° or 900°C. *in vacuo*.

As seen from table 1, the activated charcoal loses an appreciable fraction of its activity merely upon standing.

Three samples of Dr. Harmon's redwood charcoal were sealed in glass tubes with air at atmospheric pressure immediately after activation. At

this time, their activities were 31.7, 34.5, and 56.6 per cent, respectively. The first had been activated at 722°C. at 14 mm., the second at 860°C. at atmospheric pressure, and the third at 685°C. in air and then again at

TABLE 1

The activity of redwood charcoal heated for six hours at a fixed temperature in a current of air at low pressure

TEMPERATURE	PER CENT BURNED	"ACTIVITY"		PER CENT DECREASE
		Harmon	Sessions*	
340	16.5	30.7	24.3	21
368	22.5	37.9	28.8	24
400	32.8	32.8	27.1	17
514	30.0	24.9	15.7	37
590	27.5	23.7	10.5	56
720	35.0	20.6	7.6	63
730	26.5	19.6	16.0	18
800	36.5	37.6	29.8	23
865	36.0	36.1	37.6	
960	37.5	32.4		

* Original activity was determined by Harmon at the time of activation. Sessions' determinations were made after keeping four months in glass-stoppered bottles. One sample of Harmon's redwood charcoal with an original activity of 17.1 per cent was tested by one of us (R. F. S.) after standing for over two years in a corked tube and found to have an activity of 13.64 per cent, or a decrease of 21 per cent.

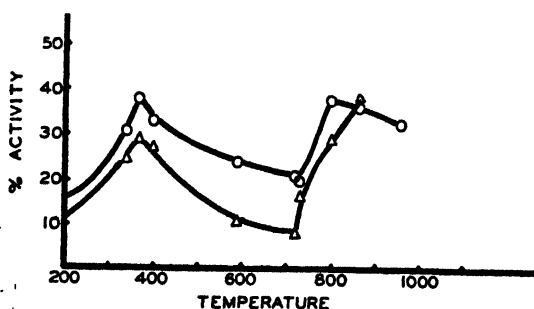


FIG. 1. Redwood charcoal. O, original activity; Δ, activity after four months

1000°C. in nitrogen. Twenty-eight months later these tubes were opened and the charcoals again tested. All three samples showed a distinct loss in activities, which were 18.06, 19.2, and 45.8 per cent, or a decrease of 43, 44, and 19 per cent, respectively.

ACTIVATION OF SUGAR CHARCOAL

For temperatures below 1000°C., platinum- or nichrome-wound resistance furnaces were used. For those above 1000°C. a small inclined hydrogen arc induction furnace, and for the highest temperatures a large induction furnace with vertical graphite vessel were employed. Temperatures below 1100°C. were measured with calibrated thermocouples, those above with the standardized optical pyrometer.

Sugar charcoal may be made as highly activated as any wood charcoal. It also exhibits its optimum activation at just over 900°C.

The results of the air activation of sugar charcoals (Nos. 1, 2, and 4) are shown in figure 2. All except four of these results were obtained in a stationary furnace inclined at an angle of 30° at atmospheric pressure.

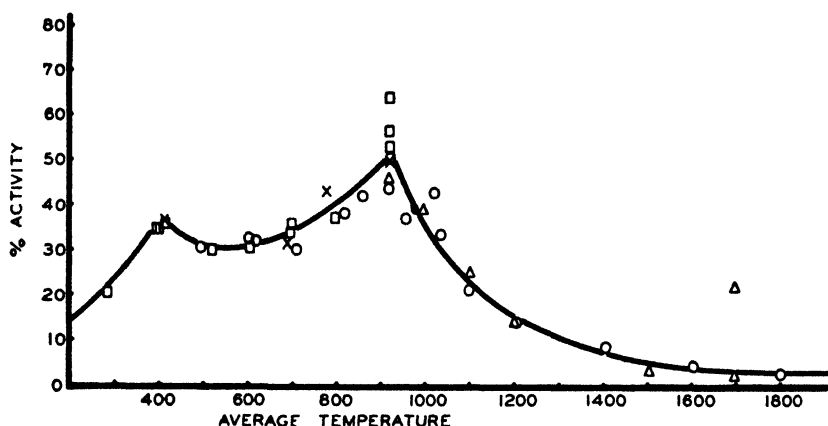


FIG. 2. Sugar charcoal. ○, charcoal No. 1 in inclined furnace; △, charcoal No. 2 in inclined furnace; □, charcoal No. 4 in inclined furnace; X, charcoal No. 4 in horizontal rotary furnace.

Usually the heating lasted one hour, but in a few cases this was extended to from two to five hours. Usually the charcoal lost from 13 to 30 per cent of its weight. Four samples of charcoal No. 4 were activated in a horizontal rotary furnace (2), with results which fully confirm the existence of the two peaks. Two other experiments, not shown on the graph for lack of space, yielded 3.0 per cent at 2014°C. and 0.5 per cent activity at 2530°C., 14 per cent being burned in each case as in the experiment at 1804°C.

It is of great interest and some significance that a specimen of charcoal No. 1 that had been air "activated" by heating for 15 minutes at 2187°C., which reduced its activity from 21.6 per cent to only 3.0 per cent, upon being air-activated again for 80 minutes at 920°C. was restored to 6.1 per cent, with a loss of one-quarter of its weight.

A series of specimens of charcoal No. 2 were also activated in a stationary horizontal furnace, with results somewhat less satisfactory than in the inclined and rotary types, yet still showing a definite peak at about 920°C. These results are plotted in figure 3, which also shows two attempts to activate charcoal No. 2 in a stationary vertical furnace, with very mediocre success. All of the results shown in this figure were obtained after runs of approximately one hour at atmospheric pressure.

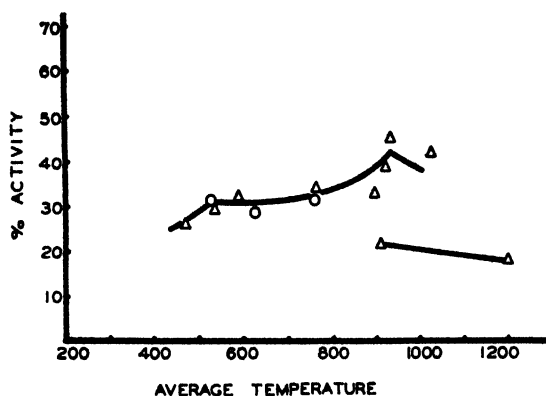


FIG. 3. Sugar charcoal in horizontal furnace. O, charcoal No. 1; Δ, charcoal No. 2. Short lower curve shows results in vertical furnace.

TABLE 2
Nitrogen activation of sugar charcoal

TEMPERATURE	FURNACE	LOSS OF WEIGHT	ACTIVITY
°C.		per cent	per cent
500	Horizontal	14.0	14.6
600	Horizontal	22.0	28.2
697	Horizontal	27.0	24.2
793	Horizontal	30.0	22.5
894	Horizontal	29.0	22.2
949	Horizontal	29.0	12.3
1000	Horizontal	28.0	11.5
1190	Vertical	29.6	5.4
1600	Vertical	28.0	1.6

Similar heating in a current of nitrogen instead of air also activated charcoal No. 2 at temperatures up to 1000°C., but the activities shown in table 2 lie well below those given for air in figure 3. The activities fall from a peak value of 28.2 per cent at 600°C. to 1.6 per cent at 1600°C.

Charcoal No. 3, originally carbonized at 900°C., which has heretofore been thought to destroy the ability to be activated, showed a surprising degree of activation at 920°C. when one sample reached a peak of 58.5

per cent after being heated for three hours in an inclined furnace at atmospheric pressure. Other activities are mentioned in the discussion.

In a few tests of the activity of the charcoals in figure 3, using phenol instead of iodine, it was found that the values were parallel with those shown for iodine. Krczil (4) states that sorption of phenol likewise runs parallel with sorption of mercuric chloride and of benzoic acid.

DISCUSSION

The experiments indicate that charcoal is better activated in air at atmospheric pressure than in nitrogen. A good flow of air rids the charcoal of volatile matter and usually shortens the time of activation. In some experiments active charcoal, activated at over $900^{\circ}\text{C}.$, on subsequent heating at $365^{\circ}\text{C}.$ lost from one-third to one-half of its activity, whereas charcoal graphitized at $2187^{\circ}\text{C}.$ was partially restored at $920^{\circ}\text{C}.$ Again, a mixture of samples of charcoal No. 3, activated at 600° and $920^{\circ}\text{C}.$, which then had an activity of 43.5 per cent, upon heating at $210^{\circ}\text{C}.$ with 10 liters of air with 3.0 per cent loss of weight, lost activity, being reduced to only 30.5 per cent. Presumably the loss of activity which occurs on standing at room temperature is greatly accelerated at $210^{\circ}\text{C}.$

Temperature is apparently the most important determining factor in the degree of activation. It is also important that the charcoal lose at least 10 or 12 per cent of its weight. Further loss of weight is distinctly advantageous, but does not have so great an effect. Presumably, the shorter the time of heating, all other factors such as per cent loss in weight being kept constant, the better the activation, or, rather, the less the concurrent inactivation. At low temperatures loss of weight is slow or opposed by another concurrent process, so that, for example, in a series of 10-g. samples of charcoal No. 3, one at $255^{\circ}\text{C}.$, over which was passed 3000 cc. of air in the course of one hour, neither gained nor lost weight, but yielded an activity of 22.4 per cent; at $450^{\circ}\text{C}.$ 2 per cent was burned and the activity was 26.2 per cent. When 3 per cent loss of weight was brought about by using 10,000 cc. of air in 80 minutes at $210^{\circ}\text{C}.$, the activity became 30.5 per cent. Five per cent loss at $695^{\circ}\text{C}.$ gave 26.3 per cent activity and at $980^{\circ}\text{C}.$ gave 35.0 per cent, while the use of 30,000 cc. of air at $600^{\circ}\text{C}.$ gave a loss of weight of 23 per cent and an activity of 41.0 per cent. Here, clearly, the factor of initial loss of weight outweighs all effect of temperature. Then at $920^{\circ}\text{C}.$ losses of 4, 10, 12, and 28 per cent in weight brought about with steadily increasing supplies of air (3000 to 28,000 cc.) gave activities of 29, 45, 46, and 58.5 per cent, although the respective times were 17, 120, 70 and 190 minutes. A temperature of approximately $920^{\circ}\text{C}.$ for a period of one hour gave consistently good results in an inclined or rotary furnace. The most promising method is to heat the charcoal at $920^{\circ}\text{C}.$ for two or even three periods of one hour each, with a period of

about twelve hours at room temperature and exposure to air between each heating.³

Olin, Lykins, and Muro (10) have very recently described a series of peat charcoals activated "in different gaseous media" at temperatures between 450° and 925°C. There is a peak at 850°C. for adsorption of air or carbon dioxide or for velocity of cataphoretic migration. This activity peak at 850°C. is several times greater than at 450°C.

Roychoudhury (11) found that sugar charcoal was more active when activated in small quantities at 900°C. for four hours, instead of at 600°C. Longer heating greatly diminished the activity. Shorter periods were not studied.

Referring to figure 1, activated charcoal shows a large loss in activity merely on being kept in a stoppered bottle⁴ or in a sealed tube. Such unused samples may lose from 30 to 60 per cent of their activity. This is in striking contrast to the constant activity preserved by activated sugar charcoal when it is sealed up with saturated organic vapors, showing no change even over periods of many years (9). The large adsorbed organic molecules serve as wedges to hold open the structure, whereas in the charcoal, merely exposed to enclosed air, the residual valencies of the carbon atoms, which must remain partially unsatisfied on account of steric hindrance (7), cause a shrinking or compacting of the porous structure.

CONCLUSIONS

1. There are two optimum temperatures at which sugar or redwood charcoal may be activated in a current of air, one at 350° to 450°C., and a still better one at 920° to 960°C.

2. Contrary to usual opinion or description, it has been found that sugar charcoal originally "carbonized" at 900°C. may still be activated. Activities as high as 58.5 per cent were obtained with sugar charcoal prepared ostensibly at this temperature. Sugar passed through the electric arc may then be air-activated.

3. When kept over a long period of time, even in sealed tubes, our charcoals show a decrease in activity of from 17 to 63 per cent. This is in great contrast to similar charcoal which has sorbed organic vapors and is kept in contact with the vapor. Then the charcoal loses none of its activity over a period of many years.

4. Although a stationary horizontal furnace may be used to activate charcoal with a fair degree of success, a stationary furnace inclined at an angle of 60° was found to give consistently better results, while a horizontal rotating furnace as used by Dubinin was the most promising of all.

³ For a more detailed examination of the effect of degree of burning see B. Bruns and O. Zarubina (*Kolloid-Z.* **64**, 279 (1933)).

⁴ See the similar observations of J. B. Firth (*J. Chem. Soc.* **119**, 929 (1921)).

5. Charcoal attains a much higher degree of activity when activated in air than when merely heated in nitrogen or helium.

6. Temperature, loss of weight (especially the first fraction), and duration of heating are the most important considerations in activating charcoal in a current of air.

Our sincere thanks are due to the California and Hawaiian Sugar Refining Corporation Ltd., to the Air Reduction Corporation of Los Angeles, to the Western Precipitation Company of Los Angeles, and to Mr. J. C. Bauer for courtesies and facilities extended.

REFERENCES

- (1) BACH, N., AND LEWITIN, I.: *Kolloid-Z.* **64**, 22 (1933).
- (2) DUBININ, M.: *Z. physik. Chem.* **150A**, 146 (1930).
- (3) HOLMES, H. N.: *Laboratory Manual of Colloid Chemistry*, p. 183. John Wiley and Sons, New York (1934).
- (4) KRCZIL, F.: *Untersuchung und Bewertung technischer Adsorptionsstoffe*. Akademische Verlagsgesellschaft, Leipzig (1931).
- (5) KRCZIL, F.: *Kolloid-Z.* **55**, 366 (1931); **64**, 123 (1933).
- (6) LAMB, A. B., WILSON, R. E., AND CHANEY, N. K.: *J. Ind. Eng. Chem.* **11**, 420 (1919).
- (7) MCBAIN, J. W.: *The Sorption of Gases and Vapours by Solids*. Geo. Routledge and Sons, Ltd., London (1932).
- (8) MCBAIN, J. W., LUCAS, H. P., AND CHAPMAN, P. F.: *J. Am. Chem. Soc.* **52**, 2668 (1930).
- (9) MCBAIN, J. W., AND SESSIONS, R. F.: *J. Am. Chem. Soc.* **56**, 1 (1934).
- (10) OLIN, H. L., LYKINS, J. D., AND MURO, W. P.: *Ind. Eng. Chem.* **27**, 692 (figure 8) (1935).
- (11) ROYCHOUDHURY, S.: *J. Indian Chem. Soc.* **8**, 440 (1931).
- (12) THOMAS, A. W.: *Colloid Chemistry*, p. 298. McGraw-Hill Book Co., New York (1934).

THE MECHANISM OF THE PHOTOCHEMICAL REACTION BETWEEN BROMINE AND WATER

H. ARMIN PAGEL AND WARNER W. CARLSON

Chemical Laboratory of the University of Nebraska, Lincoln, Nebraska

Received December 12, 1935

The mechanism of the photochemical reaction between bromine and water, which yields hydrobromic acid and oxygen, apparently has never been studied. Several qualitative experiments, however, are given in the literature. Balard (1) states that bromine water exposed to sunlight slowly decolorizes with the formation of hydrobromic and bromic acids. Löwig (4), however, found that the reaction products are hydrobromic acid and oxygen. Pebal (5) found that saturated bromine water in a sealed container does not appreciably decolorize after three months exposure to sunlight. He was unable to detect any increase of gaseous pressure upon opening the container; however the solution was found to be slightly acid and gave a positive test for bromide. Joseph (2) showed that only 2 per cent of the theoretical amount of hydrobromic acid is formed if bromine water is exposed to sunlight for over one month in colorless glass bottles. The results of the quantitative investigation carried out in this laboratory are described below.

MATERIALS AND APPARATUS

Water was prepared by distilling tap water from alkaline permanganate, followed by redistillation. To oxidize possible volatile organic matter, the water was further treated with a small portion of pure bromine and allowed to stand in sunlight for several hours. The bromine was then completely boiled out and the residue distilled, and the distillate finally redistilled. A 12-liter, all Pyrex glass still was used. Grasselli's c.p. hydrochloric acid was likewise treated with bromine, followed by gentle boiling and aeration to remove the bromine. Mallinckrodt's c.p. bromine was purified by agitating with potassium bromide solution for several hours, followed by five washings with conductivity water in a separatory funnel. To remove small amounts of insoluble impurity the bromine was then dissolved in a large volume of conductivity water and reclaimed by distillation, using the still previously mentioned. The purification was completed by distilling once from concentrated sulfuric acid and finally redistilling. Upon evaporation, the bromine left no residue and gave

negative tests for sulfuric acid. Sodium thiosulfate solutions, 0.05 *N* and 0.12 *N*, were prepared from Baker's c.p. analyzed chemical. Mallinckrodt's "Reagent quality" potassium iodide was used. This showed no trace of iodate. In order to duplicate titration conditions, the temperature of the iodine solutions to be titrated was controlled to $20 \pm 2^\circ\text{C}$., and a mechanical stirrer operating at constant speed was used.

The photochemical reactions were carried out in Pyrex reaction chambers resembling a volumetric pipet. These had a capacity of about 55 cc., and were 15 cm. in length by 25 mm. in diameter. A 4 cm. x 5 mm. tube was sealed on one end, and a 6 cm. x 11 mm. tube was sealed on the other end. The reaction chambers were cleaned with sulfuric acid-dichromate cleaning solution, thoroughly washed, and finally steamed. Accurately weighed amounts of bromine were dispensed in small sealed glass bulbs. A 200-watt, frosted, Mazda electric light bulb was used as the light source. This was mounted vertically and rotated mechanically at about 20 R.P.M. to provide average uniform illumination in a horizontal plane. The photochemical reactions were carried out in a photographic dark room, with temperatures thermostatically controlled to $25.0 \pm 0.5^\circ\text{C}$.

PROCEDURE

The smaller tube on the reaction chamber was first sealed. The bromine bulb was then introduced into the chamber through the larger tube, followed by a solid glass plunger 8 cm. long by 6 mm. in diameter. A measured amount of water (45 cc.) was then added. The larger tube was then heated well away from the open end and drawn to a slender curved constriction. This was then connected to an aspirator pump for several minutes and sealed, while evacuated, at the constricted point. By quickly inverting the reaction chamber the glass plunger was allowed to strike and break the bulb, thus liberating the bromine into the water. The reaction tubes were then mounted vertically, equidistant from the light source. The amount of reaction which had taken place during the various time intervals was then found by iodometrically determining the amount of bromine remaining. The following technique was used to avoid loss of bromine vapor: A file mark was cut about 1 cm. from the sealed end of the smaller tube on the reaction chamber, and a calcium chloride tube was connected by means of a rubber coupling. One gram of potassium iodide in 10 cc. of 0.5 *N* hydrochloric acid was then added into the calcium chloride tube. By applying transverse pressure the tube was broken at the file mark, thereby forming a valve within the rubber coupling. After the iodide solution had been introduced into the reaction chamber, the latter was vigorously shaken to extract all of the bromine vapor in the free space. The reaction chamber was then lowered into a 500-cc. Erlenmeyer flask

containing 200 cc. of 0.1 *N* hydrochloric acid and 1 g. of potassium iodide. By applying firm downward pressure the curved constricted end of the larger tube was then broken open against the bottom of the flask. This now permitted free drainage and thorough rinsing of the reaction chamber. The liberated iodine was then immediately titrated with thiosulfate. The latter was always standardized immediately after completing the analyses as follows: Weighed amounts of bromine in the sealed glass bulbs were introduced into a 500-cc. glass-stoppered Erlenmeyer flask containing the same volume of acid solution and potassium iodide as used in the analysis. The tightly stoppered flask was then vigorously shaken to break the bromine bulb and also insure complete reaction of the bromine vapor before titration.

TABLE 1
Reaction between bromine and water

SERIES A			SERIES B			SERIES C		
Time in hours	Bromine reacted*	$K \times 10^{-8}$	Time in hours	Bromine reacted*	$K \times 10^{-8}$	Time in hours	Bromine reacted*	$K \times 10^{-8}$
12	1 51	0 89	12	1 26	1 42	12	1 75	1 30
24	2 28	0 91	24	1 85	1 34	24	2 97	1 48
60	3 49	0 91	48	2 72	1 36	48	4 05	1.48
108	4 58	0 96	96	3.72	1 38	96	5 05	1.41
180	4 82	0 87	180	4 51	1 34	144	5 79	1.44

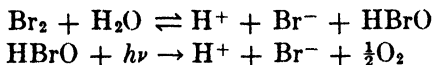
* Calculated to moles per liter $\times 10^{-4}$.

EXPERIMENTAL

Three series of experiments were carried out: series A, using 0.0221 *M* bromine at 50 cm. from the light source; series B, using 0.0221 *M* bromine at 71 cm.; and series C, using 0.0469 *M* bromine at 50 cm. The data and reaction velocity constants found are tabulated in table 1.

DISCUSSION

The reaction appears to take place as follows:



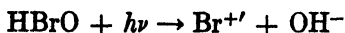
The reaction velocity constants given above were determined as follows: The initial concentrations of hypobromous and hydrobromic acids were calculated from the hydrolysis equilibrium equation (3)

$$\frac{[\text{H}^+][\text{Br}^-][\text{HBrO}]}{[\text{Br}_2]} = K_{\text{eq.}} = 5.8 \times 10^{-9}$$

The number of moles of hydrobromic acid formed at any stage of the reaction always equals twice the moles of bromine reacted, as determined iodometrically. Since the hydrolysis reaction rapidly attains equilibrium (3), the concentrations of both hypobromous and hydrobromic acids can be calculated by inserting $\{[\text{HBr}]_{\text{initial}} + [\text{HBr}]_{\text{formed}}\}$ into the hydrolysis equilibrium equation. By integrating the curves $[\text{HBrO}]/[\text{H}^+][\text{Br}^-]$, it was found that the reaction velocities can be expressed:

$$-d[\text{Br}_2]/dt = IK[\text{HBrO}]/[\text{H}^+][\text{Br}^-]$$

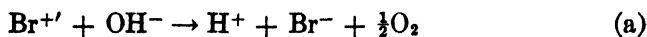
The following mechanism appears logical:



therefore,

$$-d[\text{Br}^{+'}]/dt = Ik[\text{HBrO}]$$

The $\text{Br}^{+'}$ reacts simultaneously,



and



From reaction a,

$$-d[\text{Br}^{+'}]/dt = k'[\text{Br}^{+'}][\text{OH}^-]$$

Within the range studied, the bromine concentrations remain practically constant, owing to the reversal of the hydrolysis reaction with increasing hydrobromic acid concentrations, therefore we may assume

$$-d[\text{Br}^{+'}]/dt = k''[\text{Br}^{+'}][\text{Br}^-]$$

for reaction b. The mole fractions of $\text{Br}^{+'}$ taking part in the competing reactions a and b are thus directly proportional to $k'[\text{OH}^-]$ and $k''[\text{Br}^-]$, respectively. The rate equation may then be written

$$-d[\text{Br}_2]/dt = IK[\text{HBrO}][\text{OH}^-]/[\text{Br}^-]$$

to explain the observed decrease in reaction rate with respect to the increasing concentrations of hydrobromic acid.

SUMMARY

1. The photochemical reaction between bromine and water has been studied.

2. The reaction velocity equation was found, and a reaction mechanism shown to be in logical agreement with it has been discussed.

REFERENCES

- (1) BALARD, A. J.: Ann. chim. phys. **32**, 364 (1826).
- (2) JOSEPH, A. F.: J. Soc. Chem. Ind. **29**, 1190 (1910).
- (3) LIEBHAFSKY, H. A.: J. Am. Chem. Soc. **56**, 1504 (1934).
- (4) LÖWIG, C.: Das Brom und seine chemischen Verhältnisse, p. 22. Heidelberg, 1829.
- (5) PEBAL, L.: Ann. **231**, 148 (1885).

THE DIELECTRIC CONSTANTS OF SOLUTIONS OF SOME ORGANIC ACIDS IN ETHYL ALCOHOL AND BENZENE¹

ROBERT C. GORE AND H. T. BRISCOE

*Laboratory of Inorganic and Theoretical Chemistry, Indiana University,
Bloomington, Indiana*

Received January 2, 1936

There are factors influencing the production of mobile ions other than the partial dissipation of the forces of interionic attraction in the solute through the orientation of the polar molecules of the solvent. The dielectric constant, however, measured at the proper frequency, is a measure of this factor of the ionizing power of a solvent that is due to the dissipation of interionic forces by the molecules of the solvent, through their orientation. In any theory proposing to establish a relationship that quantitatively describes the behavior of ionic solutes, the dielectric constant cannot be neglected. In modern theories it is assumed that the dielectric constant of the solvent remains unchanged in the presence of the intense electrical field surrounding each ion of the solute. It is doubtful that this assumption is justified. It might be well to consider briefly the effect of strong electric fields on the dielectric constant of a polar solvent.

Debye has derived an expression that indicates that the mean moment of a polar molecule tends to reach a saturation value as the field intensity is increased (5). If the dielectric constant of a liquid is to be considered, it will make a difference whether we have present a small electrical field or a more intense one. If we measure the dielectric constant of a liquid in the presence of a strong, constant, superimposed field, we should expect a decrease in the dielectric constant, inasmuch as the strong, superimposed field, in itself, will have brought the mean electric moment of the liquid molecules nearer the electrical saturation value.

Usually we are not concerned with electrical saturation effects because of the small field intensities. In the presence of ions, however, the electrical saturation effects are of importance. In the case of water as the solvent containing a number of ions we have the equation

$$E = e/r^2\epsilon$$

¹ This article is part of a thesis submitted to the Graduate School of Indiana University by Robert C. Gore in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1933.

where E is the field intensity, e is the ionic charge, r is the ionic radius, and ϵ is the dielectric constant. If we take $r = 10^{-7}$ cm., $\epsilon = 80$, and $e = 4.77 \times 10^{-10}$ we get

$$E = \frac{4.77 \times 10^{-10}}{80 \times 10^{-14}} = 590 \text{ E.S.U.}$$

or 177,000 volts per centimeter, which is a great enough field intensity to cause appreciable saturation effect.

If the solution contains a number of ions, there will be a region around each ion containing electrically saturated water. If now a small field is superimposed in order to measure the dielectric constant of the solution, there will be, around the ions, regions of water molecules which cannot be oriented because of electrical saturation. Consequently, we may think of the solution as containing cavities of dielectrically inactive material. The radii of these cavities will depend upon the extent of the electrical saturation.

If ethyl alcohol is used as the solvent, owing to its less ability to absorb or dissipate energy as evidenced by its lower dielectric constant, the saturation effect caused by a single ion is greater. In this case

$$E = \frac{4.77 \times 10^{-10}}{24 \times 10^{-14}} = 2070 \text{ E.S.U.} = 594,000 \text{ volts per cm.}$$

Provided that there are the same number of ions in the alcoholic solution as in the water solution, the effect of electrical saturation would be approximately four times as great in alcohol as in water.

An approximate picture of what takes place around each ion and throughout the solution has been drawn by Debye. For small concentrations of ions in aqueous solutions, experiments seem to indicate that the apparent dielectric constants of solutions containing ions diminish with the increasing concentration and e^* , the apparent dielectric constant, may be expressed by an equation such as:

$$e^* = e (1 - \gamma C)$$

where e is the dielectric constant of the pure solvent, C is the concentration in moles per liter, and γ is a constant dependent upon the ionogen and the solvent.

The decrease of the apparent dielectric constant of the solution from that of the pure solvent can be accounted for by the introduction of highly charged ions, which electrically saturate the solvent and produce cavities of dielectrically inactive solvent throughout the main body of the solution. As the number of ions increases, however, a minimum in the apparent, or macroscopic, dielectric constant is reached, and then an increase is obtained. This increase can be thought of as due to the formation of

electrical doublets or ionic dipoles between the ions as they increase in concentration and thus are forced into closer proximity. Several investigators have measured the dielectric constants of solutions of electrolytes by several methods and have obtained results which, in general, follow the theory only qualitatively. There are some exceptions to the theory even in qualitative agreement of the experimental results. The theory calls for a minimum in the apparent dielectric constant. Carman (4), however, in checking the results of Blüh (2) finds that urea continuously increases the apparent dielectric constant of an aqueous solution as the concentration is increased. Carman has also studied the effect of binary salts such as barium chloride and has found that their behavior is much more complex than the theory of Debye and Walden would lead one to believe. Other investigators have found points of inflection in the curves of other electrolytes dissolved in water.

It has been our purpose to determine the effect of the concentration of various ionogens on the apparent dielectric constant of alcoholic and, in some cases, benzene solutions. The relatively low conductivity, as compared with water solutions, of alcoholic solutions was expected to decrease the difficulties of measurement to such an extent that common methods of measuring the dielectric constants of solutions, with proper precautions, could be employed.

EXPERIMENTAL METHOD

At present impedance bridge networks and resonance or heterodyne circuits are used to measure the dielectric constants of liquids. We used both systems to obtain some of our measurements, but we made most of them with an impedance bridge. This bridge was an equal-arm, 1000-cycle, Vreeland oscillator-actuated network constructed from Leeds and Northrup's parts according to the principles laid down by Jones and Josephs (7). The precautions mentioned by Ball (1) were observed also.

Three cells were used for the measurements. The cell used in most of the measurements was made of two concentric platinum cylinders 70 x 12 mm. and 70 x 16 mm. enclosed in a Pyrex bulb fitted with side arms for filling and suitable mercury cups for electrical contact. The capacitance of this cell was determined by calibration with benzene, having a dielectric constant of 2.2725, and was found to be 24.3887 mmf. The second cell was a silver-plated, radio, variable condenser mounted so that no solid dielectric came into contact with the solutions. The third cell was a slightly modified copy of Ball's (1) best cell. During all measurements, the cells were immersed in a constant-temperature bath filled with water or transformer oil at 25°C.

All readings of refractive index were made with a Pulfrich refractometer and are for the D line of sodium.

PURIFICATION OF MATERIALS

The absolute alcohol was made from commercial 95 per cent alcohol by three treatments with lime, which was activated by heating the hydrated lime in an electric furnace to just below the sintering temperature. The aldehydes were removed by lead acetate or by sodium hydroxide and lead dioxide. When the alcohol was ready to be used, it was first distilled through a four-bulb fractionating column in order to remove the major portion of lime. It was then fractionated twice through a sixteen-bulb Young fractionating column, the first and last fractions being discarded. The purity of the alcohol was determined through the use of Schiff's reagent, aluminum ethylate, and transformer oil and by the measurement of its dielectric constant and refractive index. Various other methods of purification were tried, but none yielded as pure a product as the one used.

The anhydrous benzene was prepared from Mallinckrodt's crystallizable thiophene-free benzene by adding 20 g. of phosphorus pentoxide per liter and allowing the mixture to stand for several months. The anhydrous benzene was distilled from the phosphorus pentoxide and twice fractionated through a sixteen-bulb Young column, only the middle fraction being saved. The boiling points were determined and checked against the variations of the vapor pressure with temperature as given by Smith and Menzies (8).

The various solutes were either from the Eastman Kodak Company or from Dr. Theodor Schuchardt and were the purest obtainable. Their purity was checked by determinations of their melting points. Each solute was dried over phosphorus pentoxide, over calcium chloride, or in a vacuum. Solids having a sufficiently high melting point were dried in an electric oven at 110°C. for several hours.

PREPARATION OF SOLUTIONS

A 0.1 molar solution of each solute was prepared by weight. Other concentrations were prepared from these solutions by careful dilution. All solutions were kept in desiccators until they were measured, which was as soon as possible after preparation.

RESULTS

The results of the measurement of the dielectric constants of alcohol and benzene solutions of various organic acids are given in tables 1 and 2. The dielectric constants are referred to air as unity and are probably correct to the first decimal place, and in some instances are correct to the second decimal. The dielectric constants of solutions exhibiting values above 30 are not as accurate as the lower values, owing to errors introduced in assuming that the equivalent shunt capacitance of the cell is its true capacitance when the parallel resistance becomes relatively small, which is the

TABLE 1

Dielectric constants of solutions of organic acids in ethyl alcohol

ACID	CONCENTRATION OF ACID IN MILLIGRAM-MOLES PER LITER							
	0	1	5	10	15	20	50	100
Benzoic.....	24.47	25.34		25.57				26.73
<i>m</i> -Chlorobenzoic.....	24.31	27.12		50.77	78.70	111.5		> 110
<i>o</i> -Chlorobenzoic.....	24.18	24.35	25.29	24.74	25.21	25.97		34.70
<i>p</i> -Chlorobenzoic.....	24.43	24.33	24.72	24.36	24.51		26.97	28.02
<i>p</i> -Nitrobenzoic.....	24.34	24.81	25.36	25.70	26.72	28.78	39.04	56.87
<i>o</i> -Nitrobenzoic.....	24.27	24.85	25.26	26.37	27.88	29.14	42.16	69.23
<i>m</i> -Nitrobenzoic.....	24.21	24.77	26.34	29.10	32.72	37.37	74.22	> 115
<i>p</i> -Aminobenzoic (impure alcohol).....	26.39	26.43	26.54	26.51	26.59	26.72	26.94	28.72
<i>m</i> -Aminobenzoic.....	24.81	25.37	26.32	29.18	30.58	33.71	61.75	> 115
<i>o</i> -Aminobenzoic.....	26.21	27.43	29.04	31.90	34.72	38.94		> 115
<i>p</i> -Hydroxybenzoic.....	24.79	24.99	27.84	33.12	38.47	44.48	96.00	> 115
<i>m</i> -Hydroxybenzoic.....	23.91	25.41	25.54	25.90	26.05	26.63	28.31	32.98
<i>o</i> -Hydroxybenzoic.....	24.24	25.73	24.46	24.56	24.76	25.09	26.70	30.85
<i>o</i> -Toluic.....	24.36	24.22	24.50	24.83	24.83	26.06	27.21	30.83
<i>m</i> -Toluic.....	24.43	24.68	31.32	45.82	64.25	81.44		> 156
<i>p</i> -Toluic.....	24.09	24.37	24.6	24.79	25.05	24.81	26.54	29.38
Propionic.....	24.30	24.21	24.40	24.36	24.66	24.65	25.28	25.28
<i>n</i> -Butyric.....	24.20	24.39	24.28	24.08	24.46	24.36	24.57	25.12
Isobutyric.....	24.30	24.34	24.40	24.58	24.74	24.56	24.71	25.53
<i>n</i> -Valeric.....	24.42	24.43	24.32	24.18	24.46	24.36	24.79	25.61
Isovaleric.....	24.38	24.34	24.26	24.35	24.34	24.54	24.73	25.37
<i>n</i> -Caproic.....	24.27	24.48	24.34	24.44	24.44	24.44	25.61	27.43
Isocaproic.....	24.29	24.37	24.08	24.65	24.83	25.08	26.85	32.86
Acetic.....	24.37	24.36	24.57	24.81	25.10	24.99	25.37	26.24

TABLE 2

Dielectric constants of solutions of acids in benzene

CONCENTRATION OF ACIDS IN MILLIGRAM-MOLES PER LITER	<i>m</i> -NITROBENZOIC ACID	<i>m</i> -TOLUIC ACID	ISOCAPROIC ACID
0	2.273	2.273	2.273
5			2.274
10	2.288	2.281	2.274
15			2.273
20	2.305	2.282	2.273
50		2.283	2.279
68.07	2.377		
100		2.289	

case with the more highly conducting solutions. Even in the extreme cases, with very high dielectric constants, the error should not be greater than 2 or 3 per cent.

CONCLUSIONS

We find that ten of the solutes show, with increasing concentrations of their solutions, minima in the values of the dielectric constants. These ten solutes also show minima in the values of the refractive index and maxima in the values for the balancing resistances at the concentrations exhibiting the minima in the dielectric constants. Tables of these values have not been included for lack of space. Four other solutions show minima in the dielectric constants and refractive indices or resistances, but not in all three of these variables.

TABLE 3
Dielectric constants of solutions of organic acids

ACIDS SHOWING MINIMA IN THE CONCENTRATION, DIELECTRIC CONSTANT, REFRACTIVE INDEX, AND RESISTANCE FUNCTIONS	ACIDS SHOWING NO MINIMA IN THESE FUNCTIONS
o -Chlorobenzoic, D.E.K., R.I., R. p -Chlorobenzoic, D.E.K., R.I., R. p -Aminobenzoic, D.E.K., R.I. o -Hydroxybenzoic, D.E.K., R.I., R. o -Toluic (?), D.E.K., R.I. p -Toluic, D.E.K., R.I., R. Propionic, D.E.K., R.I., R. n -Butyric, D.E.K., R.I., R. Isobutyric, D.E.K., R.I., R. n -Valeric, D.E.K., R.I., R. Isovaleric, D.E.K., R.I., R. n -Caproic, D.E.K. (?) Isocaproic, D.E.K., R.I. Acetic, D.E.K., R.I., R.	Benzoic m -Chlorobenzoic p -Nitrobenzoic o -Nitrobenzoic m -Nitrobenzoic m -Aminobenzoic o -Aminobenzoic p -Hydroxybenzoic m -Hydroxybenzoic m -Toluic
Benzene solutions	Benzene solutions
Isocaproic, D.E.K., R.I., R.	m -Nitrobenzoic m -Toluic Benzoic

Ten acids show no minima in the dielectric constants of their solutions with increasing concentration. One solution of one acid in benzene shows minima in the dielectric constant, the refractive index, and the resistance. Three acid solutions in benzene show no minima with increasing concentration. These results are shown in table 3.

From these results our only conclusion concerning the validity of the electrical saturation theory for acids in ethyl alcohol and benzene solutions is that, although the theory may hold qualitatively in some instances, it does not hold quantitatively.

It is interesting to note that the meta-substituted benzoic acid solutions do not show minima in any case. The values for the dielectric constants

of solutions of meta-substituted acids are greater than the corresponding values for the ortho- and para-isomers.

All of the solutions of the aliphatic acids showed minima, even isocaproic acid dissolved in benzene. The stronger acids, as determined by Bright and Briscoe (3), did not show minima to any greater extent than did the weaker acids.

The *o*- and *m*-aminobenzoic acids showed no minima, while the para-isomer showed a slight minimum. In this case, however, the solutions of the para acid were measured by the heterodyne method and, in view of their conductances, their dielectric constants were subject to error. The change in the dielectric constant of the alcohol, due to the addition of equivalent quantities of the *o*- and *m*-aminobenzoic acids, was not the same for both isomers, as was found to be the case in water solutions by Hedestrand (6), who failed to obtain an increase in the dielectric constant of water by the addition of these three aminobenzoic acids.

It must be remembered that the electrical saturation theory is based upon the existence in solution of free ions carrying electrical charges. The theory has been developed from a physical viewpoint and is admittedly highly hypothetical. From our data it is obvious that the physical viewpoint is entirely inadequate in the case of acids dissolved in alcohol and even in benzene.

Other factors which would tend to change the picture as presented by the physical viewpoint would be: the possibility of the production of dipoles made up of the hydrogen ions from the acids and the hydroxyl part of the alcohol; the formation of water and ester molecules, although all determinations were made immediately after the preparation of the solutions (this is not a factor in the case of benzene solutions of the acids); the production of dipoles between the $C_2H_5OH_2^+$ ion and the negative acid radical; and the possibility that ionization is very slight and is offset by the preponderance of the undissociated molecules having large electric moments.

Inasmuch as it is difficult to find in the literature accurate values for the dielectric constant and refractive index of ethyl alcohol, it is of interest to report the following figures obtained from twenty-four samples of alcohol: dielectric constant = 24.331 at 25°C., and $n_D^{25^\circ} = 1.35921$.

REFERENCES

- (1) BALL, A. O.: J. Chem. Soc. **1930**, 571.
- (2) BLÜH, O.: Z. Physik **25**, 220 (1924).
- (3) BRIGHT, W. L., AND BRISCOE, H. T.: J. Phys. Chem. **37**, 787 (1933).
- (4) CARMAN, A. P.: Phys. Rev. **30**, 922 (1927); **31**, 157 (1928).
- (5) DEBYE, PAUL: Polar Molecules, p. 109. The Chemical Catalog Co., New York (1929).
- (6) HEDESTRAND: Z. physik. Chem. **135**, 36 (1928).
- (7) JONES, G., AND JOSEPHS, F. C.: J. Am. Chem. Soc. **50**, 1058 (1928).
- (8) SMITH, A., AND MENZIES, A.: J. Am. Chem. Soc. **32**, 1452 (1910).

THE PHYSICAL PROPERTIES OF THE TERNARY SYSTEM ETHYL ALCOHOL-GLYCERIN-WATER¹

R. C. ERNST, C. H. WATKINS, AND H. H. RUWE

Chemical Engineering Laboratories, University of Louisville, Louisville, Kentucky

Received January 2, 1936

INTRODUCTION

This and a previous investigation (10) were undertaken to obtain data to be used in the study of distillation of ternary mixtures. The densities, surface tensions, viscosities, refractive indices, and specific heats for the ternary system ethyl alcohol-glycerin-water are reported in this paper. A later paper will contain latent heats, boiling points, vapor pressures, and liquid-vapor composition data for the two ternary systems.

Densities (4), specific heats (13), refractive indices (11), and viscosities (19) of the binary system glycerin-water have been determined previously by various experimenters. The binary system ethyl alcohol-water has been investigated by Bose (6), who determined specific heats, and by Winkler (22) for density. This investigation includes the determination of densities, surface tensions, viscosities, refractive indices, and specific heats of the ternary system ethyl alcohol-glycerin-water.

EXPERIMENTAL

Materials. Glycerin of the c.p. grade was purified by repeated distillation under reduced pressure. c.p. ethyl alcohol was treated successively with metallic calcium, sodium hydroxide, and finally with metallic sodium, and distilled after each addition. The water was treated with potassium permanganate and distilled; then treated with barium hydroxide and distilled repeatedly. The physical constants of the purified materials are given in table 1.

Preparation of samples. The samples were prepared on a weight per cent basis in increments of 10 per cent. The composition of these samples is shown in table 2.

Apparatus. Densities were determined by using a Geissler pycnometer. An Ostwald-Poiseuille viscosimeter (23) was employed for the determination of viscosities. The surface tension was measured by means of the

¹ Presented before the Division of Physical and Inorganic Chemistry at the Mid-West Regional Meeting of the American Chemical Society, October 31 to November 2, 1935.

rise in a capillary tube (21). An Abbé refractometer (1) was used in obtaining refractive indices. Specific heats (17) were determined by introducing a measured quantity of electricity into the liquid and recording the temperature rise. A portable watt-second meter (Sangamo Electric Co.) and a thermometer with 0.1° graduations were used to determine these values. A carbon resistor was used as a heating element. This apparatus was inclosed in a silver-plated glass tube surrounded by an evacuated jacket.

TABLE 1
Physical constants of purified materials

MATERIAL	DENSITY	VISCOSITY	SURFACE TENSION	REFRACTIVE INDEX	SPECIFIC HEAT
Ethyl alcohol	0.7851*	1.10*	22.0*	1.3596*	0.536*
	0.78506 (14)†	1.101 (9)	22.03 (3)	1.35941 (2)	0.54 (16)
	0.78510 (22)				
Glycerin	1.2580*	934*	62.5*	1.4729*	0.555*
	1.2580 (4)	945 (19)	63.0 (8)	1.4730 (11)	0.541 (13)
	1.25802 (5)				0.589 (13)
Water	0.99707	0.893	72.0	1.3332*	1.00
	0.99707 (20)	0.894 (12)	72.0 (16)	1.3325 (15)	
	0.99707 (7)	0.893 (18)		1.3333 (10)	

* Author's experimental values.

† The numbers in parentheses refer to the bibliography.

DISCUSSION

The results of the experimental work are shown in table 3. From the data obtained, both binoidal and triangular diagrams have been drawn for each physical property. The binoidal curves are plotted with the composition of the sample on the abscissa versus the particular property under consideration as the ordinate. The constant property lines on the triangular diagrams were prepared from the binoidal curves.

Relative density. Figure 1 is a binoidal graph of the relative densities against composition. The line representing the densities of the ethyl alcohol-water system curves upward, indicating a decrease in volume upon mixing. These values agree with those of Winkler (22). The densities of the ethyl alcohol-glycerin system lie between the values for alcohol and glycerin, but likewise show a decrease in volume upon mixing. The water-glycerin curve slopes downward, denoting a slight increase in volume when mixed, agreeing with Bosart and Snoddy (4).

The constant per cent glycerin curves and the constant per cent ethyl alcohol curves show a curvature similar to the ethyl alcohol-water and the

glycerin-water curves, respectively. The characteristic curvature of the lines on the triangular diagram (figure 2) is to be expected because of the change in volume when the different components are mixed.

TABLE 2
Composition of the samples

SAMPLE NUMBER	WEIGHT PER CENT GLYCERIN	WEIGHT PER CENT ETHYL ALCOHOL	WEIGHT PER CENT WATER	SAMPLE NUMBER	WEIGHT PER CENT GLYCERIN	WEIGHT PER CENT ETHYL ALCOHOL	WEIGHT PER CENT WATER
1		100		34	50	10	40
2	100			35	40	10	50
3			100	36	30	10	60
4		10	90	37	20	10	70
5		20	80	38	10	10	80
6		30	70	39	70	20	10
7		40	60	40	60	20	20
8		50	50	41	50	20	30
9		60	40	42	40	20	40
10		70	30	43	30	20	50
11		80	20	44	20	20	60
12		90	10	45	10	20	70
13	90		10	46	60	30	10
14	80		20	47	50	30	20
15	70		30	48	40	30	30
16	60		40	49	30	30	40
17	50		50	50	20	30	50
18	40		60	51	10	30	60
19	30		70	52	50	40	10
20	20		80	53	40	40	20
21	10		90	54	30	40	30
22	10	90		55	20	40	40
23	20	80		56	10	40	50
24	30	70		57	40	50	10
25	40	60		58	30	50	20
26	50	50		59	20	50	30
27	60	40		60	10	50	40
28	70	30		61	30	60	10
29	80	20		62	20	60	20
30	90	10		63	10	60	30
31	80	10	10	64	20	70	10
32	70	10	20	65	10	70	20
33	60	10	30	66	10	80	10

Surface tension. The curve (figure 3) representing the binary system ethyl alcohol-glycerin is smooth but rises abruptly from the 80 per cent glycerin composition. The constant per cent water lines have the same characteristic curvature.

The surface tensions of the water-glycerin mixtures are between the

TABLE 3
Physical properties

SAMPLE NUMBER	DENSITY	VISCOSITY	SURFACE TENSION	REFRACTIVE INDEX	SPECIFIC HEAT
1	0.7851	1.10	22.0	1.3596	0.537
2	1.2627	934.0	62.5	1.4729	0.555
3	1.0000	0.893	72.0	1.3332	1.000
4	0.9833	1.33	46.6	1.3399	1.036
5	0.9692	1.76	37.7	1.3453	1.040
6	0.9535	2.13	32.3	1.3510	0.995
7	0.9342	2.34	29.6	1.3552	0.964
8	0.9125	2.33	28.3	1.3587	0.915
9	0.8895	2.24	26.9	1.3610	0.859
10	0.8659	2.04	26.1	1.3628	0.784
11	0.8415	1.72	25.2	1.3630	0.700
12	0.8160	1.41	24.4	1.3624	0.618
13	1.2356	155.6	64.5	1.3472	0.579
14	1.2089	55.8	65.7	1.4435	0.610
15	1.1819	18.5	66.5	1.4281	0.665
16	1.1545	9.38	66.9	1.4145	0.715
17	1.1272	5.34	67.4	1.3992	0.770
18	1.1003	3.18	67.9	1.3858	0.810
19	1.0738	2.14	68.5	1.3708	0.870
20	1.0484	1.54	69.5	1.3582	0.930
21	1.0237	1.09	70.5	1.3451	0.967
22	0.8199	1.52	22.9	1.3701	0.550
23	0.8566	2.23	23.9	1.3799	0.550
24	0.8947	3.49	24.2	1.3898	0.549
25	0.9368	5.83	25.4	1.4005	0.548
26	0.9806	10.4	26.1	1.4109	0.550
27	1.0288	20.6	27.7	1.4226	0.549
28	1.0797	45.3	29.6	1.4344	0.549
29	1.1366	103.3	32.7	1.4470	0.551
30	1.1932	254.0	38.9	1.4597	0.552
31	1.1724	74.6	40.4	1.4462	0.581
32	1.1484	26.2	39.9	1.4321	0.622
33	1.1212	14.1	40.4	1.4193	0.675
34	1.1004	7.42	41.3	1.4063	0.741
35	1.0776	4.75	42.7	1.3917	0.790
36	1.0514	3.13	44.0	1.3769	0.856
37	1.0270	2.22	45.4	1.3639	0.921
38	1.0025	1.69	46.4	1.3511	0.966
39	1.1165	41.1	32.7	1.4343	0.588
40	1.0988	16.9	33.5	1.4220	0.635
41	1.0753	9.29	34.6	1.4096	0.681
42	1.0525	5.91	34.9	1.3961	0.735
43	1.0318	4.04	35.1	1.3827	0.810
44	1.0101	2.92	35.9	1.3705	0.885
45	0.9882	2.20	37.0	1.3573	0.953
46	1.0618	19.50	30.4	1.4235	0.591

TABLE 3—*Concluded*

SAMPLE NUMBER	DENSITY	VISCOSITY	SURFACE TENSION	REFRACTIVE INDEX	SPECIFIC HEAT
47	1.0460	10.80	30.1	1.4112	0.644
48	1.0273	6.63	31.3	1.3990	0.690
49	1.0090	4.60	31.6	1.3871	0.754
50	0.9888	3.47	32.0	1.3749	0.831
51	0.9690	2.69	32.8	1.3631	0.910
52	1.0149	12.3	28.8	1.4120	0.592
53	0.9984	7.04	28.9	1.4006	0.642
54	0.9821	4.73	28.9	1.3900	0.702
55	0.9655	3.57	29.6	1.3787	0.775
56	0.9486	2.84	29.9	1.3672	0.860
57	0.9670	6.63	27.2	1.4011	0.591
58	0.9553	4.59	28.0	1.3907	0.648
59	0.9430	3.52	27.5	1.3810	0.720
60	0.9272	2.78	28.3	1.3700	0.809
61	0.9282	4.26	26.3	1.3911	0.582
62	0.9143	3.26	26.3	1.3817	0.660
63	0.9016	2.59	27.0	1.3717	0.741
64	0.8889	2.88	24.5	1.3812	0.610
65	0.8796	2.36	25.6	1.3721	0.677
66	0.8505	2.00	24.6	1.3720	0.616

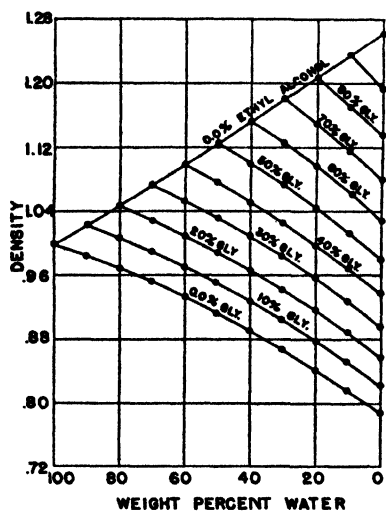


FIG. 1

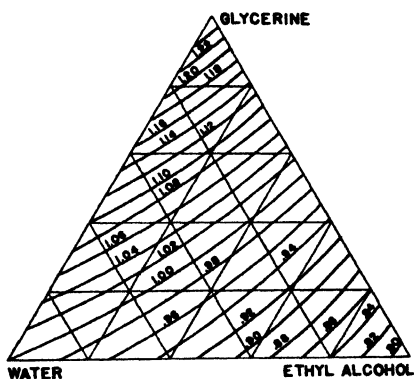


FIG. 2

FIG. 1. Relative density glycerin-ethyl alcohol-water at 25°C.

FIG. 2. Relative density glycerin-ethyl alcohol-water at 25°C.

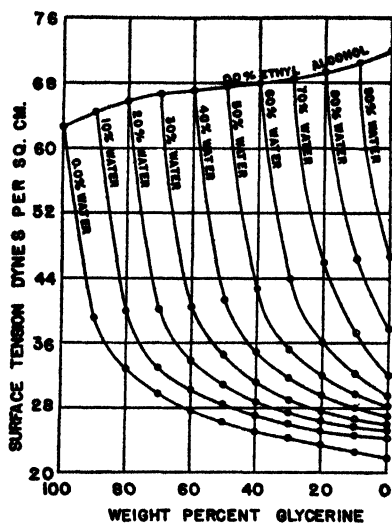


FIG. 3

FIG. 3. Surface tension glycerin-ethyl alcohol-water at 25°C.

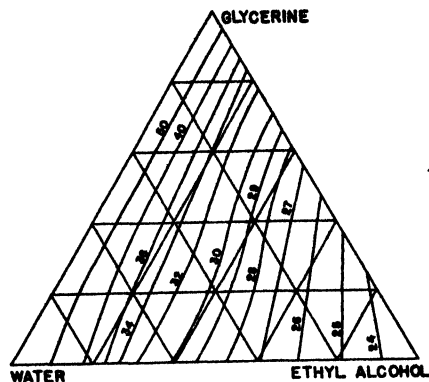


FIG. 4

FIG. 4. Surface tension glycerin-ethyl alcohol-water at 25°C.

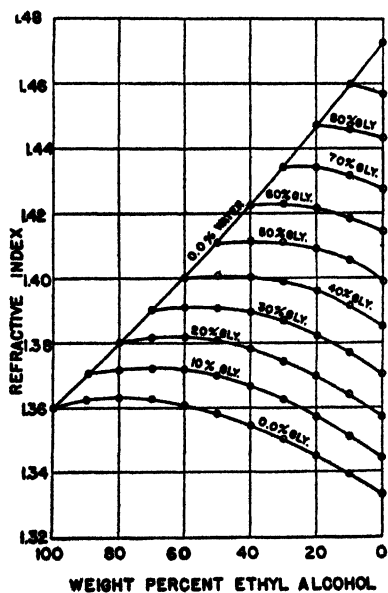


FIG. 5

FIG. 5. Refractive index glycerin-ethyl alcohol-water at 25°C.

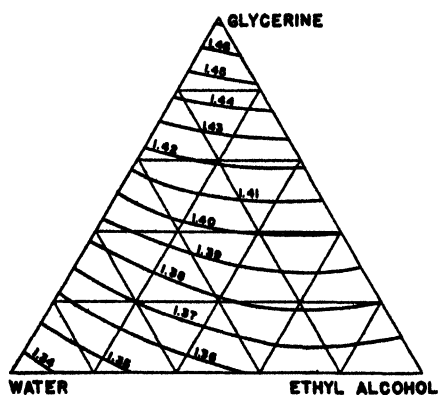
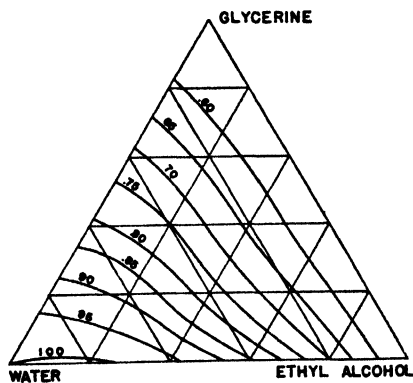
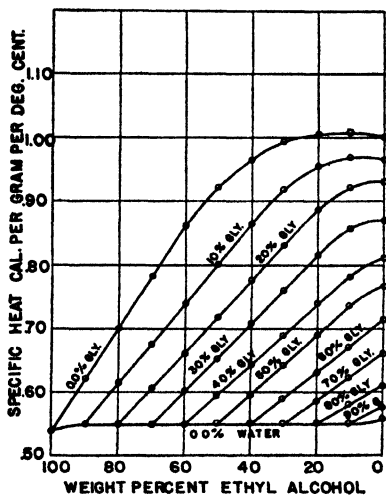
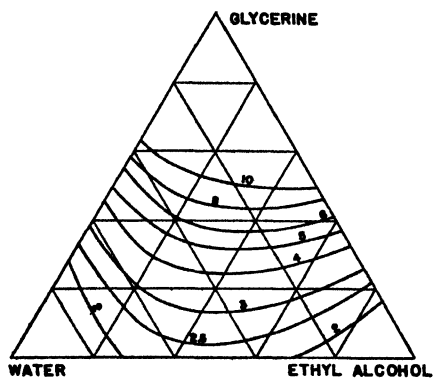
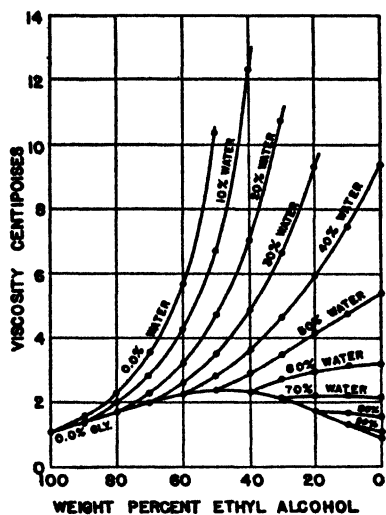


FIG. 6

FIG. 6. Refractive index glycerin-ethyl alcohol-water at 25°C.



values for the pure components; they lie on a smooth curve but not in a straight line.

In figure 4 the line representing compositions having a surface tension of 34.0 is a straight line. The lines on either side are convex with respect to this constant property line.

Refractive index. The refractive indices are shown graphically in figure 5 and figure 6. The values of the alcohol-water mixtures lie on a smooth curve reaching a maximum at 80 per cent alcohol. The constant per cent glycerin lines show similar maximum points.

The glycerin-water values curve slightly but are intermediate between the refractive indices of the pure components. The constant per cent water lines have the same curvature as the glycerin-alcohol curve. The constant property lines in figure 6 show a similar curvature throughout.

Viscosity. Because of the high viscosity of glycerin, namely 945 centipoises (19), when compared to that of alcohol and water, the curves showing viscosities include only those samples whose glycerin percentages are below 40 per cent. In figure 7 the alcohol-water mixtures have maximum viscosity at 50 per cent alcohol. The constant per cent glycerin curves show similar maximum points. These maxima explain the shape of the lines in figure 8.

Specific heat. Figure 9 shows the specific heat of the system plotted against composition. The specific heat of the water-alcohol system reaches a maximum at 80 per cent water and drops on a smooth curve to pure alcohol. The glycerin-alcohol line is almost straight. The constant per cent glycerin lines show similar curvature, but approach straight lines at 60 per cent glycerin.

The slopes of the lines on the ternary diagram (figure 10) are explained by the constant per cent glycerin lines reaching a maximum.

CONCLUSION

Densities, surface tensions, viscosities, refractive indices, and specific heats for the ternary system glycerin-ethyl alcohol-water have been determined. Both binoidal curves and ternary diagrams have been prepared for each property and are included in this paper.

REFERENCES

- (1) ABBÉ, E.: *Carls Repertarium der Physik* **15**, 643 (1879).
- (2) ANDREWS: *J. Am. Chem. Soc.* **30**, 353 (1905).
- (3) BIRCUMSHAW: *J. Chem. Soc.* **121**, 887 (1922).
- (4) BOBART AND SNODDY: *Ind. Eng. Chem.* **19**, 506 (1927).
- (5) BOBART AND SNODDY: *Ind. Eng. Chem.* **20**, 1377 (1928).
- (6) BOSE: *Z. physik. Chem.* **58**, 585 (1907).
- (7) CHAPPIUS: *Travaux et memoirs du bureau international des poids et mesures* **13**: D 40 (1907).

- (8) DRUCKER: Z. physik. Chem., Stoichiometrie und Verwandtschaftslehre **52**, 641 (1905).
- (9) DUNSTAN AND THALE: J. Chem. Soc. **95**, 1556 (1909).
- (10) ERNST, LITKENHOUS, AND SPANYER: J. Phys. Chem. **36**, 842 (1932).
- (11) IYER AND USHER: J. Chem. Soc. **127**, 841 (1925).
- (12) JAYNER: J. Chem. Soc. **121**, 1511 (1922).
- (13) MAGIE: Phys. Rev. **16**, 381 (1903).
- (14) OSBORNE, McKELVY, AND BEARCE: Bur. Standards Bull. **9**, 327 (1913).
- (15) QUINCKE: Ann. Physik **44**, 774 (1891).
- (16) RICHARDS AND CARVER: J. Am. Chem. Soc. **43**, 827 (1921).
- (17) RICHARDS AND GUCKER: J. Am. Chem. Soc. **47**, 1876 (1925).
- (18) SHEELY: Ind. Eng. Chem. **24**, 1061 (1932).
- (19) SHEELY: Ind. Eng. Chem. **24**, 1063 (1932).
- (20) THEISSEN, SCHEEL, AND DIESSELHORST: Wiss. Abhandl. physik. tech. Reichsanstalt **2**, 68 (1900).
- (21) Trans. Chem. Soc. **63**, 1089 (1873).
- (22) WINKLER: Ber. **38**, 3612 (1905).
- (23) Wiss. Abhandl. physik. tech. Reichsanstalt **4**, 241 (1901).

MIXED CRYSTAL FORMATION OF ZINC SULFIDE POSTPRECIPITATED WITH MERCURIC SULFIDE. THE AGING OF MERCURIC SULFIDE AND OF ZINC SULFIDE

R. MOLTZAU¹ AND I. M. KOLTHOFF

School of Chemistry, University of Minnesota, Minneapolis, Minnesota

Received October 17, 1935

In an extensive study regarding the postprecipitation of zinc sulfide with mercuric sulfide to be reported in this journal, it was found that the zinc sulfide could not be completely removed from the mixed precipitate by extraction with 3 *N* hydrochloric acid at room temperature. This suggested a possible mixed crystal formation of zinc sulfide with mercuric sulfide. Such a view was supported by an x-ray investigation described in this paper.

X-ray diagrams were made by the powder method, using a Siegbahn (15) metal x-ray tube with a copper target as the source of the x-rays. The finely divided materials investigated were coated on a copper wire 0.5 mm. in diameter by means of collodion. The pattern thus obtained from the copper wire provided a means of calibrating the photographic film. The lattice constant (a) of copper was taken to be 3.61 A.U. (6), and upon this value are based the corrections applied to observed values of the angles of reflection. In calculating lattice constants, only lines due to the K_{α} radiations of copper were considered.

MERCURIC SULFIDE

Mellor (13) lists four different forms in which mercuric sulfide may exist. Three of these are crystalline, while black amorphous mercuric sulfide is given as the fourth. Of the three crystalline forms reported, the existence of two, namely α -HgS or ordinary red cinnabar and α' -HgS or black meta-cinnabar, is unquestioned; these two forms have been known for a long time to exist in nature. The third crystalline form listed by Mellor is the supposed new form reported by Allen and Crenshaw (1), which is not found in nature and which is a red hexagonal form differing from cinnabar. Allen and Crenshaw based their report of the existence of this new modification on evidence gained by microscopic examination. Kolk-

¹ This article is based upon a thesis submitted by R. Moltzau to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1935.

meijer, Bijvoet, and Karssen (9), employing the powder method of x-ray investigation, found none of the modifications described by Allen and Crenshaw to contain crystals different from the ordinary black and red forms.

Cinnabar is the most commonly occurring natural form, and was considered by Allen and Crenshaw (1) to be the most stable modification at all temperatures up to the sublimation temperature (580°C.). Rinse (14), however, found that vapor pressure data indicated the existence of a transition point at about 386°C., above which the black form was the stable modification. The change in color from red to black, which takes place when cinnabar is heated under certain conditions, has been observed and reported by other investigators (1, 16).

The structure of red trigonal cinnabar has been determined by Mauguin (12) using the Bragg method of x-ray analysis, by which the dimensions of the unit cell were found to be: $a = b = 4.15$ A.U., $c = 9.51$ A.U. It was found that with a slight deviation, the particles were arranged on a rhombohedral lattice. The work was later confirmed by Kolkmeijer and coworkers (9), using the Debye-Scherrer method of x-ray analysis.

The structure and properties of natural and artificial black metacinnabarite have been investigated by various workers (7, 9, 10). There is entire agreement that the black form usually precipitated from acid solution is identical in structure with that of naturally occurring metacinnabarite, the atoms of mercury and sulfur being arranged on a face-centered cubic lattice of the zinc blende type. The edge of the unit cell is listed by Wyckoff (18) as 5.84 A.U. In agreement with this value the authors likewise determined the lattice constant to be 5.84 A.U.

Mercuric sulfide freshly precipitated from acid medium exists as very imperfect submicroscopic crystals. While Böhm and Niclassen (3) report that mercuric sulfide precipitated at 0°C. gave at once a sharp interference pattern, it was found in this work that under the conditions of radiography employed only a few diffuse interference maxima were obtained. The period of aging necessary before the precipitate achieves a condition making possible a clear pattern was, however, found to be rather short. Mercuric sulfide precipitated from a medium which was quite strongly acid (2 *N* sulfuric acid) and aged in the supernatant liquid for three days at room temperature yielded a well-defined diffraction pattern characteristic of the cubic metacinnabar form.

In general, black cubic mercuric sulfide undergoes upon aging a transformation to the red cinnabar form. The observation has previously been made that the red modification is readily formed by digestion of the black gel with soluble alkali sulfides. According to Weiser (17) this process consists in the solution of the black form, with subsequent precipitation of the less soluble red form, although no experimental proof has been given

that such a mechanism is the actual case. It was found in this work that alkalinity is not a necessary condition for the formation of the red form, but that transformation occurs upon aging in the supernatant liquid at room temperatures even in quite strongly acid medium. However, the speed of transformation decreases with increasing acidity. If the mercuric sulfide is precipitated from a neutral solution of the perchlorate and allowed to age in the resulting supernatant liquid saturated with hydrogen sulfide, transformation to the trigonal form as indicated by the color change of the precipitate is apparent within a few hours and is apparently complete within a day or two, whereas in more strongly acid solution (2 to 3 *N* sulfuric acid) a week or so will elapse before the change becomes convincingly apparent. Proof of the transformation and of the identity of the crystal forms involved was obtained by x-ray methods, as well as by visual observation of the color changes taking place. Transformation in case the precipitate is suspended in pure water or in dilute ammonium hydroxide was not detected. From the observations made, it is apparent that conversion from the cubic to the hexagonal form is hastened by low hydrogen-ion concentration, high concentration of hydrogen sulfide (or sulfide ion), and by higher temperatures of the supernatant liquid in which aging takes place. The presence of certain substances, such as potassium iodide and sodium acetate, was found to retard the transformation, as did likewise the presence of postprecipitated zinc sulfide. In the light of the proven occurrence of mixed crystal formation exhibited by mercuric sulfide and postprecipitated zinc sulfide, the fact that the latter inhibits the transformation of the former is construed as indicative of a stabilization of the metacinnabar form by virtue of the presence of zinc sulfide in the lattice.

ZINC SULFIDE

Two different crystal modifications of zinc sulfide are known to exist in nature. The regular form, or zinc blende, is by far the more abundant and is the stable form at ordinary temperatures, passing to the hexagonal or wurtzite form at or above the conversion point of 1020°C. (1). Wyckoff gives the lattice constant of the zinc blende form as 5.43 A.U. Values reported in the literature show a considerable deviation from this figure, ranging from 5.395 (4, 5) to 5.437 (10). In our work an aged precipitate of zinc sulfide yielded a value of 5.40 A.U.

Böhm and Niclassen (3) report that zinc sulfide precipitated at 0°C. from solutions of zinc sulfate was amorphous, but that after being digested on a water bath for several days, an x-radiogram of the product showed sharp interference maxima, indicating that crystallization had taken place. Likewise, in the work reported here, the diffraction pattern obtained from a product freshly precipitated at room temperature from a 0.1 *M* solution

of zinc sulfate at an initial acidity of 0.1 *N* sulfuric acid was barely visible, while that obtained employing a product precipitated under like conditions, but aged at room temperature for one month in the supernatant liquid saturated with hydrogen sulfide, was sharply defined. A marked change in solubility accompanying aging was also observed. In 2 *N* sulfuric acid saturated with hydrogen sulfide, the solubility of the fresh product was in the neighborhood of 0.035 *M*, in contrast to 0.005 *M* for the aged product. Aging in the dry condition apparently does not affect the crystalline nature of precipitates of either zinc sulfide or mercuric sulfide. After existing in a dry condition at room temperature for one year, precipitates which had been separated from the mother liquor shortly after precipitation did not yield any definite diffraction pattern.

It is generally accepted that only the more stable blende form is precipitated from alkaline solution (1, 17). However, some question arises as to the identity of the crystal form assumed by zinc sulfide precipitated from acid solution by the action of hydrogen sulfide. Levi and Fontana (11) found only the blende form to have been precipitated from solutions of the sulfate and acetate. Allen, Crenshaw, and Merwin (1) found by microscopic examination of crystals formed in sealed tubes in the presence of the supernatant liquid at temperatures between 200° and 400°C. that, while only crystals of the blende structure were formed from alkaline solution, from acid solution both the wurtzite and zinc blende forms were produced. From their investigations concerning the crystalline forms and genetic conditions of the sulfides of zinc, iron, cadmium, and mercury, they drew the general conclusion that the higher the temperature, the greater the quantity of stable form, while the higher the acidity of the solution from which precipitation takes place, the greater the quantity of the unstable form. From this generalization they were led to predict that the acid concentration required to give pure wurtzite was probably close to neutrality at ordinary temperatures. In our work an x-radiogram of the aged product previously described yielded no indication of the presence of any but the zinc blende form. The possibility of a minor percentage of the wurtzite form being present is not, however, excluded on the basis of this evidence.

Employing the values 5.84 A.U. and 5.40 A.U. as the respective lattice constants of metacinnabar and zinc blende, the difference is found to be 7.8 per cent of the average value. On the basis of the work of Havighurst, Mack, and Blake (8) and of Barth and Lunde (2) regarding the limitations of miscibility in systems of the alkali halides and the halides of monovalent copper, silver, and thallium, respectively, we should expect that at least a limited mixed crystal formation of the sulfides of mercury and zinc is possible. The possibility is further strengthened by the fact that there is a mineral, bearing the name of guadalcazarite (Hg, Zn) (S, Se) and

containing about 10 mole per cent zinc sulfide, which according to Hartwig (7) has a lattice constant of 5.781 ± 0.006 A.U.

TABLE 1

Study of a precipitate of mercuric sulfide containing postprecipitated zinc sulfide (Hg-Zn)S mounted on a copper wire for exposure. Copper radiation; 30 kv.; 10 ma.; 4 hours exposure. Diameter of specimen (S) = 0.7 mm. Diameter of camera = 57.3 mm.

LINE NO.	ESTIMATED RELATIVE LINE INTENSITY	($2d - S$) MM. 2θ (DEGREES)	2θ CALC- LATED FOR Cu LINES	2θ CORRECTED	SIN $^2\theta$	RADI- ATION	hkl
1	vw*	24.4		23.9	0.04287	K_β	111
2	s	27.0		26.5	0.05253	K_α	111
3	vw	28.8		28.3	0.05976	?	?
4	m	31.3		30.9	0.07097	K_α	200
5	m	43.7	43.3			K_α	111 (Cu)
6	s	44.7		44.3	0.14215	K_α	220
7	vw	47.7		47.3	0.16092	K_β	311
8	m	50.9	50.5			K_α	200 (Cu)
9	ms	52.7		52.3	0.19424	K_α	311
10	vw	55.3		54.9	0.21250	K_α	222
11	vw	56.8		56.3	0.22258	?	?
12	vw	65.1		64.6	0.28317	K_α	400
13	vw	66.4	65.9			K_β	220 (Cu)
14	mw	71.2		70.8	0.33557	K_α	331
15	vw*	73.2		72.8	0.35215	K_α	420
16	s	74.6	74.2			K_α	220 (Cu)
17	vw*	79.9	79.2			K_β	311 (Cu)
18	w	81.7		81.3	0.42437	K_α	422
19	w	87.7		87.3	0.47645	K_α	333 511
20	ms	90.4	90.0			K_α	311 (Cu)
21	m	95.4	95.2			K_α	222 (Cu)
22	vw	97.3		97.2	0.56267	K_β	620
23	mw	103.7		103.7	0.61842	K_α	531
24	mw	114.1		114.1	0.70417	K_α	620
25	mw	117.0	117.0			K_α	400 (Cu)
26	vw	119.1	119.2			K_β	420 (Cu)
27	s (broad)	137.0	136.6			K_α	331 (Cu)
28	s (broad)	145.2	144.8			K_α	420 (Cu)

$$\sin^2\theta = 0.017656(h^2 + k^2 + l^2). \quad a = 5.79 \text{ A.U.}$$

* Reflection appeared only on one side of the film.

A precipitate of mercuric sulfide containing postprecipitated zinc sulfide was prepared by saturating a solution which was 0.021 *M* with respect to zinc sulfate and mercuric chloride, respectively, at an acidity of 2 *N* sulfuric acid with hydrogen sulfide and allowing the mixture to stand for one month. It has been shown¹ that in this precipitation the mercuric

sulfide is first precipitated in a pure form, zinc sulfide entering the precipitate upon further standing. At the end of one month, the precipitate was filtered off, washed with water and alcohol in the order named, and dried over concentrated sulfuric acid at reduced pressure. The composition of the precipitate was determined to be 39 mole per cent zinc sulfide and 61 mole per cent mercuric sulfide. The specimen had the usual black color of metacinnabar. The diffraction pattern obtained employing this product is represented by the data in table 1. A precipitate consisting of 48 and 52 mole per cent respectively of postprecipitated zinc sulfide and mercuric sulfide precipitated from an equimolar solution of zinc sulfate and mercuric chloride at an acidity of 0.5 *N* sulfuric acid and aged for three days in the supernatant liquid, yielded a value for the lattice constant identical within experimental error with that determined employing the first described precipitate. The diffraction pattern, however, was not as sharply defined in the case of the second precipitate as in the case of the former.

Referring to the table, reflections No. 3 and No. 11 present difficulties in their interpretation. Line No. 3 assumes a value of 2θ , which is too large to allow its identification as the K_β reflection from (200) planes. Moreover with K_α as weak as 4 and 12, one would not expect the corresponding K_β reflections to be detectable. Reflections from pure zinc sulfide possessing approximately these values (No. 3 and No. 11) for 2θ are strong. Consideration of the total amount of zinc sulfide present, the fact that aging in the sense of increasing crystalline perfection may have been greatly retarded by the presence of mercuric sulfide, and finally the fact that many of the stronger reflections from zinc sulfide fall in positions very close to those occupied by lines due to the bulk of the precipitate, suggests an explanation as to why no definite evidence of a second phase consisting either of pure zinc sulfide or possibly of a very dilute solid solution of mercuric sulfide in zinc sulfide is to be found in the diffraction pattern.

The decrease in lattice constant from 5.84 A.U. to 5.79 A.U. is a strong indication that mixed crystal formation occurs. By application of the formulation by Havighurst, Mack, and Blake (8) for the general rule of additivity regarding the relation between composition and change in lattice constant as applicable to mixed crystals of cubic habit, it is indicated that mixed crystal formation takes place to the extent of about 12 mole per cent zinc sulfide.

No indication was found in this work that mixed crystals of hexagonal habit exist.

SUMMARY

1. Aging of the sulfides of zinc and mercury in the supernatant liquid at room temperature after precipitation from acid solution by hydrogen sul-

fide results in a perfection of the crystalline state, as evidenced by increased clarity and sharpness of the diffraction patterns obtained.

2. Some of the variables affecting the transformation of mercuric sulfide from the black cubic form of metacinnabar to the red trigonal form of cinnabar upon aging in the supernatant liquid have been noted.

3. Evidence has been obtained by x-ray methods that a limited mixed crystal formation to the extent of about 12 mole per cent of zinc sulfide takes place between freshly precipitated black mercuric sulfide and post-precipitated zinc sulfide.

REFERENCES

- (1) ALLEN, E. T., CRENSHAW, J. L., AND MERWIN, H. E.: *Z. anorg. allgem. Chem.* **79**, 125 (1913); **90**, 107 (1915).
- (2) BARTH, T., AND LUNDE, G.: *Z. physik. Chem.* **122**, 293 (1926).
- (3) BÖHM, J., AND NICLASSEN, H.: *Z. anorg. allgem. Chem.* **132**, 1 (1923).
- (4) DEJONG, W. F.: *Z. Krist.* **66**, 515 (1928).
- (5) GERLACH, W. VON: *Physik. Z.* **23**, 114 (1922).
- (6) GRIME, G., AND MORRIS-JONES, W.: *Phil. Mag.* [7] **7**, 1113 (1929).
- (7) HARTWIG, W.: *Sitzber. preuss. Akad. Wiss. Physik math. Klasse*, p. 79 (1926).
- (8) HAVIGHURST, R. J., MACK, E., AND BLAKE, F. C.: *J. Am. Chem. Soc.* **47**, 29 (1925).
- (9) KOLKMEIJER, N. H., BIJVOET, J. M., AND KARSEN, A.: *Rec. trav. chim.* **43**, 678, 894 (1924).
- (10) LEHMAN, W. M.: *Z. Krist.* **60**, 379 (1924).
- (11) LEVI, G. R., AND FONTANA, C. G.: *Chem. Abstracts* **22**, 3851 (1928).
- (12) MAUGUIN, C.: *Compt. rend.* **176**, 1483 (1923).
- (13) MELLOR, J. W.: *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. IV, p. 944. Longmans, Green and Co., London (1923).
- (14) RINSE, J.: *Rec. trav. chim.* **47**, 28 (1928).
- (15) SIEGBAHN: *Spectroscopy of X-rays*. Oxford University Press (1925).
- (16) SPRING, W.: *Z. anorg. Chem.* **7**, 382 (1894).
- (17) WEISER, H. B.: *The Colloidal Salts*, pp. 83, 94. McGraw-Hill Book Co., Inc., New York (1928).
- (18) WYCKOFF, R. W. G.: *The Structure of Crystals*, 2nd edition, p. 229. Chemical Catalog Co., Inc., New York (1931).

QUANTITATIVE ANALYSES OF LIESEGANG RINGS

A. T. LINCOLN AND JOHN C. HILLYER

Department of Chemistry, Carleton College, Northfield, Minnesota

Received January 11, 1936

As part of a program of careful quantitative study of the Liesegang phenomenon, we have performed analyses for the ions present in both bands and clear spaces in a copper chromate structure in silicic acid gel. By removing the banded structure from the test tube and subjecting the sections to analyses, we have shown both copper and chromate ions to be present together in the lower sections of this gel without the formation of a precipitate.

Very few studies of this type have been made. Earlier work by Hedges and Henley (1) on magnesium hydroxide made no attempt to distinguish between the soluble portion and the widely dispersed precipitate. Hughes (2) has recently made a very careful and complete survey of the distribution of ions in a large number of different systems. Our present work extends and corroborates his recent findings.

Banded structures of copper chromate were prepared by a technique previously described (3). After formation, these were removed from the tubes, cut into sections, the soluble salts extracted, and the copper, sulfate, and chromate ions determined. In all cases the copper and sulfate ions were distributed throughout the whole tube in a manner compatible with diffusion from the top, while the chromate ion was exhausted in all the upper sections. However, in most tubes both copper and chromate ions were found together in the lowest clear space, below which a band was just forming. The concentrations were such as to cause a precipitate in the absence of the gel.

Since no definite information could be found on the solubility product of this salt, tests were made to determine whether the actual concentrations found did cause a precipitate in the absence of a gel. Solutions were made which upon mixing yielded exactly the same concentrations as found. Heavy precipitates formed in all cases. Additional solutions were made containing the exact amount of free acetic acid present in the gels, and also, both the acid and the large amount of sodium acetate formed in precipitating the silicic acid. In these cases also a precipitate formed, although somewhat slowly.

For the preparation and analysis of the gels we are indebted to Mr. John Main.

EXPERIMENTAL

The gels were formed from equal volumes of 1.06 sp. gr. sodium silicate solution and 0.65 *N* acetic acid solution by a technique previously described (3). The gels were made 0.1 *M* and 0.2 *M* with respect to potassium chromate. Concentrations of 0.3 *M* and 0.4 *M* copper sulfate were used on top.

After the completion of the reaction the bottoms of the tubes were filed and cracked off. The gels were then pushed out with a rod, loosening first

TABLE 1
Results of typical analyses

REACTION	SPACE		DISTANCE FROM TOP	WEIGHT OF SAMPLE	PER CENT OF SO ₄ [—]	PER CENT OF Cu ⁺⁺	PER CENT OF CrO ₄ [—]
			<i>inches</i>	<i>grams</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
I. K ₂ CrO ₄ , 0.08 <i>M</i> ; CuSO ₄ , 0.3 <i>M</i>	1st clear space	A	$\frac{1}{2}$	1.3169	0.86	0.43	None
		B	$\frac{1}{2}$	1.4948	0.87	0.46	None
	1st band	A	1	1.2948	0.78	0.39	None
		B	1	1.4598	0.79	0.40	None
	2nd clear space	A	$1\frac{1}{2}$	4.7322	0.68	0.19	0.10
		B	$1\frac{1}{2}$	3.1824	0.68	0.19	0.12
II. K ₂ CrO ₄ , 0.2 <i>M</i> ; CuSO ₄ , 0.3 <i>M</i>	1st clear space	A	$\frac{1}{2}$	1.0689	0.69	0.28	None
		B	$\frac{1}{2}$	1.2486	0.69	0.27	None
	1st band	A	1	1.3846	0.58	0.25	None
		B	$1\frac{1}{2}$	1.3519	0.57	0.24	None
	2nd clear space	A	$1\frac{1}{2}$	3.8695	0.28	0.09	0.19
		B	$1\frac{1}{2}$	3.4502	0.29	0.09	0.18
III. K ₂ CrO ₄ , 0.1 <i>M</i> ; CuSO ₄ , 0.4 <i>M</i>	1st clear space	A	$\frac{1}{2}$	1.7517	0.83	0.39	None
		B	$\frac{1}{2}$	1.6385	0.83	0.39	None
	1st band	A	1	1.3690	0.71	0.35	None
		B	$1\frac{1}{2}$	1.4006	0.73	0.35	None
	2nd clear space	A	$1\frac{1}{2}$	4.7593	0.58	0.18	0.10
		B	$1\frac{1}{2}$	3.8891	0.58	0.20	0.08

by momentary immersion in hot water if necessary. The gel was then cut into sections by means of a razor blade. Usually two clear spaces and one ring were analyzed.

Analytical procedure

The portions selected for analysis were placed in weighing bottles and carefully weighed. The soluble salts were extracted with boiling water and filtered. The extraction was repeated five or six times.

Chromate ions were first reduced by boiling with dilute hydrochloric

acid and ethyl alcohol (4). After expelling the excess alcohol, the sulfate was precipitated as barium sulfate and weighed as such, according to the standard procedure. The filtrate from this precipitation was then treated with hydrogen sulfide to precipitate the copper, which was redissolved, and determined iodometrically. Finally, chromium was precipitated as the hydroxide, taking the usual precautions to eliminate excess ammonia, ignited to the oxide, and weighed.

The results of typical analyses are shown in table 1.

Precipitation in the absence of gel

Two solutions were made containing respectively 1.416 g. and 0.756 g. of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in 100 ml., and two solutions containing respectively 0.402 g. and 0.666 g. of K_2CrO_4 . These were twice the amounts found in the corresponding sections of the same gels. When equal volumes of the corresponding solutions were mixed, the final solutions should contain exactly the same concentrations as found in the gel. Heavy precipitates formed in both cases.

The copper sulfate solutions of the same concentration were prepared containing (1) 3.0 ml. of acetic acid per 100 ml. and (2) 7.7558 g. of $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$ and the acid as in (1). Adding these to the corresponding chromate solutions produced a heavy precipitate of copper chromate.

SUMMARY

By quantitative analyses of rhythmically banded copper chromate structures in silicic acid gel it has been shown that, while the copper and the sulfate ions are distributed throughout the tube in a manner to be expected from simple diffusion, there are present in the lower clear space both copper and chromate ions in moderate concentration.

Copper chromate has been found to precipitate when the ions are present in the concentrations found in these spaces, even in the presence of the same amount of free acetic acid and of sodium acetate present in these gels. It appears that the presence of silicic acid inhibits the precipitation of this compound until higher concentrations are reached, and so aids in the formation of banded structures.

REFERENCES

- (1) HEDGES AND HENLEY: J. Chem. Soc. **1928**, 2714.
- (2) HUGHES: Biochem. J. **28**, 1086 (1934).
- (3) LINCOLN AND HILLYER: J. Phys. Chem. **38**, 907 (1934).
- (4) SCOTT: Standard Methods of Chemical Analysis. D. Van Nostrand Co., New York (1925).

THE SOLUBILITY AND ACTIVITY COEFFICIENT OF SILVER ACETATE IN MIXED SOLVENTS¹

F. H. MACDOUGALL AND CHARLES EDWARD BARTSCH

School of Chemistry, University of Minnesota, Minneapolis, Minnesota

Received January 25, 1936

INTRODUCTION

The experimental work described in this paper was undertaken in order to furnish an additional test of the applicability of the theory of Debye and Hückel (2) to strong electrolytes dissolved in mixed solvents. With this purpose in mind, we measured the solubility of silver acetate in various mixtures of water and ethyl alcohol in the presence of various amounts of a soluble nitrate. The nitrates used were those of lithium, sodium, potassium, calcium, strontium, and barium.

The solubility of silver acetate in water at 25°C. has been determined by a number of investigators. We give herewith the results obtained in moles per liter: Raupenstrauch (10), 0.0671; Goldschmidt (3), 0.0669; Jaques (5), 0.0663; Hill and Simmons (4), 0.0667; Knox and Will (6), 0.0667; MacDougall (7), 0.0664; MacDougall and Rehner (8), 0.0663. The value obtained in the present research was 0.06634.

MATERIALS USED

The silver acetate, obtained from Mallinckrodt, was 64.62 per cent silver (theoretical, 64.64 per cent) and was used without further purification. It was kept in black lacquered bottles and stored in the dark. The nitrate salts were recrystallized from "conductivity" water and dried at 150°C. The water was "conductivity" water, prepared by distillation of distilled water in a tin-lined vessel in the presence of sodium hydroxide and potassium permanganate. The ethyl alcohol used was approximately 95 per cent by volume and was tested according to Murray (9). It was found to be free from acetone, aldehyde, other organic impurities, and heavy metals. It was used without further purification.

EXPERIMENTAL PROCEDURE

The mixed solvent was prepared by mixing weighed amounts of 95 per cent alcohol and conductivity water, but the exact alcoholic content of

¹ This paper gives the essential portions of the dissertation presented by Charles E. Bartsch to the Graduate Faculty of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1935.

the mixture was calculated from its density. Mixtures containing approximately 10, 20, and 30 per cent by weight of alcohol were used as solvents.

Weighed amounts of the solvent and of the nitrate salt were brought together in a glass-stoppered flask. When the nitrate had dissolved, equal portions of the solution were transferred to two amber-colored glass-stoppered bottles containing an excess of silver acetate. The bottles were sealed immediately with a heavy layer of paraffin. They were then rotated end over end in a water bath at $25.00 \pm 0.05^\circ\text{C}$. for at least forty-eight hours. For the purpose of sampling, the bottles were removed from the rotator and clamped upright and almost completely immersed in the bath. After half an hour, the paraffin was removed from the stopper, a siphon (containing a small cotton wad in the "bottle" end) was inserted in the liquid, and about 125 cc. of the liquid was blown by compressed air into a 250-cc. Erlenmeyer flask, immersed as completely as was permissible in the water bath. The Erlenmeyer flask was fitted with a rubber stopper to minimize evaporation. From this flask two samples of 50 cc. each were withdrawn by means of an accurately calibrated pipet and weighed in glass-stoppered weighing bottles. Results for density and for analysis were accordingly obtained in quadruplicate for each concentration of added nitrate.

The solutions containing 10 or 20 per cent alcohol were analyzed gravimetrically for silver; all other solutions were analyzed volumetrically. The volumetric analysis was carried out by the Volhard method for silver as suggested by Professor I. M. Kolthoff. The samples were transferred to 250-cc. Erlenmeyer flasks, acidified with 5 cc. of concentrated nitric acid, and diluted to 100 cc. Then 5 cc. of ferric nitrate indicator solution was added. The solutions were titrated immediately with 0.04 *N* potassium thiocyanate to a reddish-brown coloration. The solutions were then shaken until the color disappeared. The titration with potassium thiocyanate was continued until a faint rose coloration remained after vigorous shaking. The thiocyanate solution was standardized with a solution containing a known amount of silver acetate. The standardization was checked with a solution containing a known weight of silver nitrate.

METHODS OF EXPRESSING COMPOSITION OF THE SOLUTIONS

If p is the fraction of alcohol in the mixed solvent, the number of moles of water, $N_{\text{H}_2\text{O}}$, and of ethyl alcohol, $N_{\text{C}_2\text{H}_5\text{OH}}$, in 1000 g. of solvent can be found from the equations

$$\begin{aligned} N_{\text{H}_2\text{O}} &= \frac{1000(1-p)}{18.015} \\ N_{\text{C}_2\text{H}_5\text{OH}} &= \frac{1000p}{46.045} \end{aligned} \quad (1)$$

The molar concentration, c , of a solute salt is the number of moles of the salt in a liter of the solution. The molal concentration, m , is the number of moles in 1000 g. of mixed solvent. In calculating the mole fraction of a component of the solution we have assumed that the dissolved silver acetate and added nitrate salt are completely ionized. If x is the mole fraction of Ag^+ or of $\text{C}_2\text{H}_3\text{O}_2^-$ in a solution in which the molalities of silver acetate and added nitrate are m and m_s , respectively, then

$$x = \frac{m}{N_{0_1} + N_{0_2} + 2m + \nu m_s} \quad (2)$$

where ν is the number of ions obtainable on complete ionization of one molecule of added nitrate salt.

The density of the solvent (alcohol-water mixture) is represented by d_0 , that of the solution saturated with silver acetate and containing various amounts of nitrate salt by d .

ACTIVITY COEFFICIENTS

If f , γ , and γ_c are the mole-fraction, molality, and molarity activity coefficients respectively of any solute then

$$\gamma = \frac{f}{1 + \frac{2m + \nu m_s}{N_{0_1} + N_{0_2}}} \quad (3)$$

$$\gamma_c = \frac{d_0}{d} \left(1 + \frac{mM + m_s M_s}{1000} \right) \gamma \quad (4)$$

M and M_s are the molecular weights of silver acetate and added nitrate salt, respectively.

According to Debye and Hückel (2), the activity coefficient of a univalent ion (or of a uni-univalent salt) at 25°C. is given by the equations

$$\log_{10} f = \log_{10} x_0 - \log_{10} x = - \frac{BS^{\frac{1}{2}}}{1 + AS^{\frac{1}{2}}} \quad (5)$$

$$B = \frac{352.61}{D^{\frac{1}{2}}} \quad (6)$$

$$A = \frac{2.914 \times 10^8}{D^{\frac{3}{2}}} a \quad (7)$$

where D is the dielectric constant of the solvent and a is a suitable mean ionic diameter. In equation 5, x is the mole fraction of silver ion in a given saturated solution and x_0 is the extrapolated value of x for an ionic strength equal to zero; in other words, x_0 is the activity of silver ion in any solution saturated with silver acetate.

The dielectric constant of an alcohol-water mixture was calculated by linear interpolation from the values given by Åkerlöf (1).

EXPERIMENTAL DATA

In table 1 we give the solubility at 25°C. of silver acetate in alcohol-water mixtures containing from 0 to 50 per cent ethyl alcohol. In tables

TABLE 1

Solubility at 25°C. of silver acetate in mixtures of ethyl alcohol and water

PER CENT ALCOHOL	DENSITY OF SATURATED SOLUTION	MOLAR CONCENTRATION OF SILVER ACETATE	PER CENT ALCOHOL	DENSITY OF SATURATED SOLUTION	MOLAR CONCENTRATION OF SILVER ACETATE
0.00	1.0048	0.0663	25.06	0.9616	0.0294
5.00	0.9955	0.0577	29.82	0.9530	0.0251
7.62	0.9898	0.0523	30.05	0.9526	0.0249
9.00	0.9882	0.0506	40.27	0.9323	0.0180
15.03	0.9784	0.0413	50.14	0.9102	0.0124
19.96	0.9696	0.03			

TABLE 2

Solubility at 25°C. of silver acetate in mixtures of ethyl alcohol and water containing potassium nitrate

9.41 PER CENT ALCOHOL D = 73.14			20.37 PER CENT ALCOHOL D = 66.78			30.02 PER CENT ALCOHOL D = 61.09		
m KNO ₃	Satd. soln.	$10^3 \times Ag^+$	m KNO ₃	Satd. soln.	$10^3 \times Ag^+$	m KNO ₃	Satd. soln.	$10^3 \times Ag^+$
0.0	0.9875	0.9649	0.0	0.9709	0.7449	0.0	0.9520	0.5811
0.05131	0.9909	1.0311	0.05006	0.9742	0.8196	0.04949	0.9581	0.6488
0.09865	0.9939	1.0710	0.09945	0.9776	0.8612	0.09996	0.9615	0.6910
0.2004	1.0010	1.1333	0.1998	0.9838	0.9191	0.2004	0.9669	0.7506
0.3006	1.0075	1.1751	0.2982	0.9897	0.9623	0.3007	0.9728	0.7974
0.4057	1.0153	1.2190	0.3958	0.9952	0.9892	0.3990	0.9774	0.8298
0.5012	1.0174	1.2462	0.4959	1.0009	1.0271	0.4984	0.9838	0.8591
0.6013	1.0271	1.2662	0.5994	1.0070	1.0507	0.6265	0.9906	0.8931
0.8046	1.0381	1.3114	0.7923	1.0180	1.0925	0.8813	1.0028	0.9452
1.0049	1.0495	1.3517	0.9898	1.0281	1.1285	1.0365	1.0103	0.9705
1.2957	1.0655	1.3868	1.2539	1.0422	1.1686			
1.6227	1.0828	1.4313	1.4916	1.0540	1.1964			

2 to 7 we give the solubility in the presence of added nitrates in solvents containing approximately 10, 20, and 30 per cent ethyl alcohol. The data are also represented graphically in figures 1, 2, and 3. An examination of the tables and of the figures will show that the solubility of silver acetate increases with the concentration of added nitrate, and that for a solution

of a given ionic strength the effect of a given nitrate is given in general by the order $\text{KNO}_3 < \text{NaNO}_3 < \text{Ba}(\text{NO}_3)_2 < \text{Sr}(\text{NO}_3)_2 < \text{LiNO}_3 < \text{Ca}(\text{NO}_3)_2$.

TABLE 3

Solubility at 25°C. of silver acetate in mixtures of ethyl alcohol and water containing sodium nitrate

9.17 PER CENT ALCOHOL $D = 73.27$			20.37 PER CENT ALCOHOL $D = 66.78$			30.02 PER CENT ALCOHOL $D = 61.09$		
m_{NaNO_3}	Satd. soln	$10^3 \times \text{Ag}^+$	m_{NaNO_3}	Satd. soln	$10^3 \times \text{Ag}^+$	m_{NaNO_3}	Satd. soln	$10^3 \times \text{Ag}^+$
0.0	0.9879	0.9815	0.0	0.9709	0.7449	0.0	0.9520	0.5811
0.04711	0.9910	1.0485	0.04819	0.9735	0.8141	0.05054	0.9558	0.6452
0.09579	0.9948	1.0892	0.09547	0.9762	0.8591	0.1002	0.9590	0.6931
0.1911	1.0001	1.1548	0.1937	0.9823	0.9251	0.2011	0.9652	0.7565
0.2864	1.0047	1.2009	0.2880	0.9859	0.9652	0.3012	0.9704	0.8066
0.3859	1.0102	1.2395	0.3821	0.9921	1.0023	0.3996	0.9745	0.8375
0.4702	1.0147	1.2660	0.4776	0.9971	1.0355	0.5001	0.9800	0.8757
0.5822	1.0206	1.3042	0.5738	1.0022	1.0637	0.6014	0.9856	0.9060
0.7735	1.0309	1.3464	0.7626	1.0116	1.1103	0.8003	0.9948	0.9573
0.9579	1.0405	1.3826	0.9571	1.0214	1.1557	0.9983	1.0048	0.9990
1.1903	1.0522	1.4123	1.1894	1.0336	1.1923	1.3025	1.0192	1.0594
1.4411	1.0644	1.4466	1.4258	1.0437	1.2327	1.6015	1.0343	1.1034
1.9095	1.0861	1.4934	1.8935	1.0646	1.2920	2.0047	1.0509	1.1583
2.3876	1.1077	1.5292	2.3764	1.0861	1.3353			
2.8732	1.1284	1.5555	2.8061	1.1047	1.3659			

TABLE 4

Solubility at 25°C. of silver acetate in mixtures of ethyl alcohol and water containing barium nitrate

9.17 PER CENT ALCOHOL $D = 73.27$			19.39 PER CENT ALCOHOL $D = 67.35$			30.02 PER CENT ALCOHOL $D = 61.09$		
$m_{\text{Ba}(\text{NO}_3)_2}$	Satd. soln	$10^3 \times \text{Ag}^+$	$m_{\text{Ba}(\text{NO}_3)_2}$	Satd. soln	$10^3 \times \text{Ag}^+$	$m_{\text{Ba}(\text{NO}_3)_2}$	Satd. soln	$10^3 \times \text{Ag}^+$
0.0	0.9879	0.9815	0.0	0.9722	0.7456	0.0	0.9520	0.5811
0.02541	0.9941	1.0877	0.01036	0.9749	0.8013	0.01028	0.9568	0.6328
0.05050	0.9994	1.1412	0.02463	0.9780	0.8506	0.01978	0.9589	0.6684
0.1012	1.0107	1.2326	0.05384	0.9842	0.9226	0.04002	0.9628	0.7229
0.1454	1.0198	1.2824	0.1241	0.9986	1.0235	0.06038	0.9669	0.7643
0.2021	1.0314	1.3462				0.08023	0.9711	0.7979
0.2343	1.0381	1.3798				0.09930	0.9748	0.8274
0.2978	1.0456	1.4187						

APPLICATION OF THE DEBYE-HÜCKEL THEORY

Values of A and x_0 of equation 5 were obtained for each series of solutions by substituting in the equation the observed values of x and $S^{\frac{1}{2}}$ for two

TABLE 5

Solubility at 25°C. of silver acetate in mixtures of ethyl alcohol and water containing strontium nitrate

9.90 PER CENT ALCOHOL D = 72.86			19.95 PER CENT ALCOHOL D = 67.03			30.45 PER CENT ALCOHOL D = 60.83		
m Sr(NO ₃) ₂	d Satd. soln.	$10^3 \times \text{Ag}^+$	m Sr(NO ₃) ₂	d Satd. soln.	$10^3 \times \text{Ag}^+$	m Sr(NO ₃) ₂	d Satd. soln.	$10^3 \times \text{Ag}^+$
0.0	0.9866	0.9565	0.0	0.9712	0.0742	0.0	0.9534	0.5781
0.02672	0.9912	1.0664	0.02730	0.9768	0.8505	0.01236	0.9557	0.6425
0.05250	0.9964	1.1258	0.05039	0.9808	0.9202	0.02495	0.9581	0.6872
0.09925	1.0045	1.2116	0.09969	0.9893	1.0074	0.04085	0.9604	0.7305
0.1991	1.0206	1.3441	0.1988	1.0041	1.1348	0.07072	0.9858	0.7918
0.2986	1.0370	1.4381	0.2997	1.0210	1.2345	0.09976	0.9706	0.8403
0.4018	1.0530	1.5189	0.3973	1.0362	1.3162	0.2019	0.9865	0.9685
0.4995	1.0685	1.5898	0.4986	1.0514	1.3913	0.2998	1.0007	1.0711
0.5978	1.0832	1.6486	0.5965	1.0658	1.4620	0.4018	1.0163	1.1591
0.8013	1.1135	1.7717	0.7974	1.0950	1.5890	0.6033	1.0453	1.3073
1.0021	1.1425	1.8844	0.9896	1.1214	1.6968	0.7999	1.0722	1.4536
1.2463	1.1764	2.0015	1.2403	1.1561	1.8414	0.9954	1.0994	1.5780
1.4855	1.2088	2.0959	1.5377	1.1950	1.9961	1.4888	1.1651	1.8837
2.0065	1.2746	2.3012	1.9768	1.2497	2.1990			

TABLE 6

Solubility at 25°C. of silver acetate in mixtures of ethyl alcohol and water containing lithium nitrate

9.41 PER CENT ALCOHOL D = 73.14			19.39 PER CENT ALCOHOL D = 67.35			30.02 PER CENT ALCOHOL D = 61.09		
m LiNO ₃	d Satd. soln.	$10^3 \times \text{Ag}^+$	m LiNO ₃	d Satd. soln.	$10^3 \times \text{Ag}^+$	m LiNO ₃	d Satd. soln.	$10^3 \times \text{Ag}^+$
0.0	0.9883	0.9647	0.0	0.9722	0.7456	0.0	0.9520	0.5811
0.05177	0.9909	1.0412	0.05225	0.9746	0.8232	0.04890	0.9550	0.6557
0.1018	0.9931	1.0877	0.09767	0.9767	0.8692	0.10622	0.9572	0.7097
0.2017	0.9977	1.1625	0.2030	0.9813	0.9479	0.19890	0.9606	0.7712
0.2991	1.0019	1.2192	0.2973	0.9855	0.9961	0.2979	0.9650	0.8217
0.4082	1.0062	1.2718	0.4053	0.9894	1.0433	0.3881	0.9685	0.8621
0.5092	1.0103	1.3103	0.5114	0.9936	1.0861	0.4969	0.9728	0.9047
0.6191	1.0145	1.3507	0.5981	0.9969	1.1191	0.5977	0.9764	0.9417
0.8042	1.0219	1.4178	0.7966	1.0042	1.1830	0.7969	0.9836	1.0085
1.0214	1.0303	1.4781	0.9913	1.0117	1.2422	0.9974	0.9912	1.0721
1.3229	1.0415	1.5552	1.2529	1.0213	1.3111	1.3072	1.0031	1.1552
1.6556	1.0536	1.6310	1.5749	1.0328	1.3915	1.5735	1.0119	1.2284
2.1024	1.0693	1.7288	1.9670	1.0462	1.4911	1.9970	1.0257	1.3294
2.5195	1.0836	1.8260	2.5001	1.0640	1.6226			
3.0930	1.1027	1.9543	3.0096	1.0809	1.7457			

TABLE 7

Solubility at 25°C. of silver acetate in mixtures of ethyl alcohol and water containing calcium nitrate

9.90 PER CENT ALCOHOL <i>D</i> = 72.86			19.95 PER CENT ALCOHOL <i>D</i> = 67.93			30.45 PER CENT ALCOHOL <i>D</i> = 60.83		
$\text{Ca}(\text{NO}_3)_2$	Satd. soln.	$10^3 \times \text{Ag}^+$	$\text{Ca}(\text{NO}_3)_2$	Satd. soln.	$10^3 \times \text{Ag}^+$	$\text{Ca}(\text{NO}_3)_2$	Satd. soln.	$10^3 \times \text{Ag}^+$
0.0	0.9857	0.9565	0.0	0.9712	0.7420	0.0	0.9534	0.5781
0.02581	0.9908	1.0758	0.02404	0.9754	0.8643	0.01338	0.9554	0.6548
0.04913	0.9935	1.1466	0.04886	0.9789	0.9394	0.02549	0.9575	0.7046
0.09891	1.00004	1.2510	0.09900	0.9848	1.0411	0.04072	0.9592	0.7524
0.1966	1.0118	1.4229	0.2022	0.9971	1.2199	0.07269	0.9626	0.8328
0.3028	1.0245	1.5420	0.3008	1.0085	1.3342	0.10118	0.9664	0.8929
0.3967	1.0354	1.6396	0.3938	1.0190	1.4418	0.1997	0.9775	1.0501
0.4956	1.0469	1.7366	0.4932	1.0313	1.5361	0.2974	0.9883	1.1749
0.6006	1.0586	1.8219	0.5919	1.0407	1.6241	0.4010	0.9997	1.2905
0.8013	1.0798	1.9879	0.7914	1.0615	1.8033	0.5994	1.0203	1.4818
0.9916	1.1002	2.1386	0.9958	1.0828	1.9712	0.7996	1.0409	1.6677
1.2375	1.1252	2.3090	1.2466	1.1074	2.1742	0.9991	1.0606	1.8486
1.5338	1.1544	2.5202	1.4687	1.1285	2.3428	1.4869	1.1056	2.2750
2.0224	1.1994	2.8394	1.9823	1.1759	2.7582			

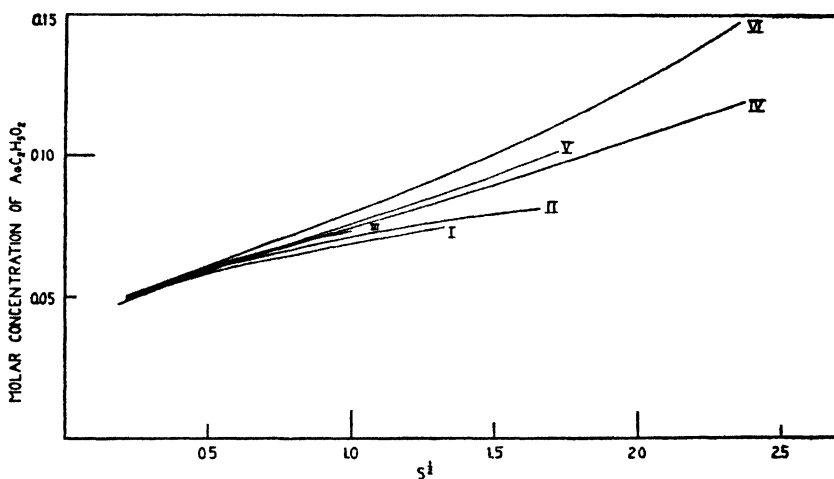


FIG. 1. Solubility of silver acetate in about 10 per cent alcohol in the presence of various nitrates. I. KNO_3 ; solvent, 9.41 per cent alcohol. II. NaNO_3 ; solvent, 9.17 per cent alcohol. III. $\text{Ba}(\text{NO}_3)_2$; solvent, 9.17 per cent alcohol. IV. $\text{Sr}(\text{NO}_3)_2$; solvent, 9.90 per cent alcohol. V. LiNO_3 ; solvent, 9.41 per cent alcohol. VI. $\text{Ca}(\text{NO}_3)_2$; solvent, 9.90 per cent alcohol.

solutions, one of which was always the solution that contained no added nitrate salt. From the two simultaneous equations so obtained, a value of A and a value of x_0 were calculated. We have summarized in table 8

the results of these calculations. One might infer from this table that the Debye-Hückel equation is in general valid up to approximately the same

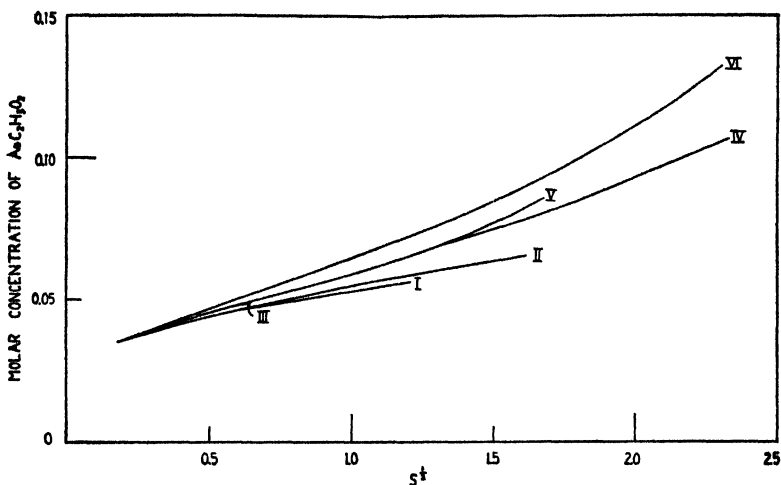


FIG. 2. Solubility of silver acetate in about 20 per cent alcohol in the presence of various nitrates. I. KNO_3 ; solvent, 20.37 per cent alcohol. II. NaNO_3 ; solvent, 20.37 per cent alcohol. III. $\text{Ba}(\text{NO}_3)_2$; solvent, 19.39 per cent alcohol. IV. $\text{Sr}(\text{NO}_3)_2$; solvent, 19.95 per cent alcohol. V. LiNO_3 ; solvent, 19.39 per cent alcohol. VI. $\text{Ca}(\text{NO}_3)_2$; solvent, 19.95 per cent alcohol.

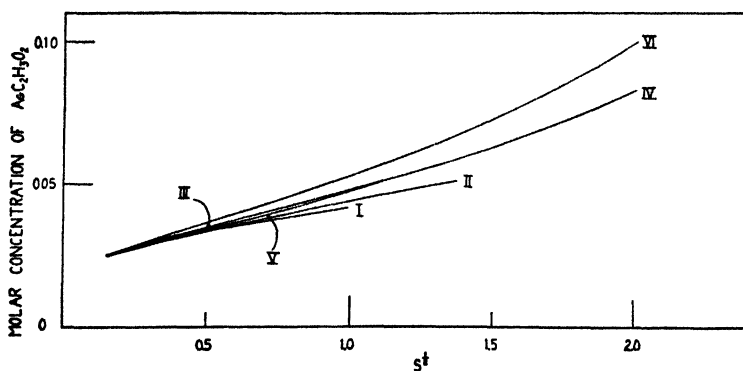


FIG. 3. Solubility of silver acetate in about 30 per cent alcohol in the presence of various nitrates. I. KNO_3 ; solvent, 30.02 per cent alcohol. II. NaNO_3 ; solvent, 30.02 per cent alcohol. III. $\text{Ba}(\text{NO}_3)_2$; solvent, 30.02 per cent alcohol. IV. $\text{Sr}(\text{NO}_3)_2$; solvent, 30.45 per cent alcohol. V. LiNO_3 ; solvent, 30.02 per cent alcohol. VI. $\text{Ca}(\text{NO}_3)_2$; solvent, 30.45 per cent alcohol.

ionic strength, irrespective of the nature of the added nitrate. For higher ionic strengths, there are marked differences in the effects of different

nitrates. In the case of the less soluble barium nitrate, the validity of the Debye-Hückel equation extends up to solutions saturated with this salt. For all other nitrates investigated (except sodium nitrate in 9.17 per cent alcohol) there is a falling off in the calculated values of A when we go to solutions of higher ionic strengths than those given in table 8, but whereas this decrease in A is relatively slow when sodium nitrate and potassium nitrate are the added salts, it is more rapid in the case of strontium nitrate and lithium nitrate and still more so for calcium nitrate. It would therefore be more correct to say that the range of *approximate* validity of equation 5 is greatest for sodium nitrate and potassium nitrate, less for strontium nitrate and lithium nitrate, and least for calcium nitrate.

As will be pointed out in a later publication from this laboratory, the great increase in solubility of silver acetate in the presence of calcium nitrate is probably due to the formation of the intermediate ion CaOAc^+ .

TABLE 8
Calculated values of A and x_0

ADDED NITRATE	ca. 10 PER CENT $\text{C}_2\text{H}_5\text{OH}$			ca. 20 PER CENT $\text{C}_2\text{H}_5\text{OH}$			ca. 30 PER CENT $\text{C}_2\text{H}_5\text{OH}$		
	A	10^3x_0	Valid to an ionic strength	A	10^3x_0	Valid to an ionic strength	A	10^3x_0	Valid to an ionic strength
KNO_3	1.43	0.775	0.5	1.37	0.597	1.0	1.39	0.466	0.6
NaNO_3	1.28	0.783	2.65	1.31	0.596	0.9	1.34	0.466	0.8
$\text{Ba}(\text{NO}_3)_2$	1.14	0.778	0.9	1.08	0.593	0.8	1.20	0.464	0.75
$\text{Sr}(\text{NO}_3)_2$	1.08	0.758	0.9	1.02	0.588	0.88	1.08	0.459	0.75
$\text{Li}(\text{NO}_3)_2$	1.14	0.766	0.8	1.10	0.593	0.85	1.23	0.464	0.75
$\text{Ca}(\text{NO}_3)_2$	0.86	0.750	0.9	0.75	0.582	0.98	0.80	0.455	0.75

Since the solvents referred to as approximately 10 per cent alcohol varied appreciably in composition (e.g., 9.17, 9.41, and 9.90 per cent alcohol) the calculated values of 10^3x_0 in table 8 for these solvents are not expected to be identical. Moreover the extrapolated value of x_0 depends somewhat on the value of A used in equation 5. If we assume that the value of x_0 and the value of the solubility, x , of silver acetate in a mixed solvent vary relatively in the same way with the per cent of alcohol, and if we take as most reliable the values of x_0 obtained in the presence of sodium nitrate, potassium nitrate, and barium nitrate, we readily find the following relation for the value of x_0 as a function of the per cent, p , of alcohol when p is in the neighborhood of 10 per cent; viz.,

$$10^3x_0 = 0.760 + 0.026(10 - p)$$

This relation gives

$$10^3x_0 = 0.783, \text{ for } p = 9.17 (\text{NaNO}_3, \text{Ba}(\text{NO}_3)_2)$$

$$10^3x_0 = 0.776, \text{ for } p = 9.41 (\text{KNO}_3, \text{LiNO}_3)$$

$$10^3x_0 = 0.767, \text{ for } p = 9.90 (\text{Sr}(\text{NO}_3)_2, \text{Ca}(\text{NO}_3)_2)$$

The solvents richer in alcohol differ relatively so little from exactly 20 per cent and 30 per cent, respectively, that we may infer from table 8 (giving greatest weight to the results with sodium nitrate and potassium nitrate) that

$$10^3x_0 = 0.596, \text{ for } p = 20 \text{ per cent alcohol}$$

$$10^3x_0 = 0.466, \text{ for } p = 30 \text{ per cent alcohol}$$

TABLE 9
Values of a in A.U.

PER CENT $\text{C}_2\text{H}_5\text{OH}$	VALUES OF a	
	KNO_3	NaNO_3
0 0	4.35	3.69
10.0	4.21	3.86
20.0	3.85	3.67
30.0	3.91	3.62

TABLE 10
Activity coefficient of silver acetate in saturated solutions at 25°C .

SOLVENT	10^3x_0	m_0	C_0	f
Water.....	0.960	0.0533	0.0531	0.800
10 per cent alcohol.....	0.760	0.0396	0.0388	0.797
20 per cent alcohol.....	0.596	0.0291	0.0281	0.803
30 per cent alcohol.....	0.466	0.0211	0.0201	0.802

IONIC DIAMETERS

The values of A obtained by application of equation 5 can be interpreted in terms of average ionic diameters, a , by means of equation 7. In table 9 we give the values of a so obtained for solutions containing potassium nitrate and sodium nitrate, respectively. The values of a for 0 per cent alcohol are taken from the papers by MacDougall (7) and MacDougall and Rehner (8).

ACTIVITY COEFFICIENTS

The mean activity coefficient, f , of silver acetate is given by the ratio $\frac{x_0}{x}$. The activity coefficients, γ and γ_c , may be calculated by means of equations 3 or 4 or from the equations

$$\gamma = \frac{m_0}{m}$$

$$\gamma_c = \frac{c_0}{c}$$
(8)

where $m_0 = (N_{01} - N_{02})x_0$ (see equation 11) and $c_0 = d_0m_0$; d_0 is the density of the solvent. It will be observed that we have assigned a value of unity to the activity coefficient of an ion in any of our solvents (water, 10 per cent, 20 per cent, or 30 per cent alcohol) when the ionic strength approaches zero. We give in table 10 values of the mean activity coefficients of silver acetate in saturated solutions of that salt when the solvent is water, 10 per cent, 20 per cent, and 30 per cent alcohol, respectively. For the data in aqueous solutions containing no alcohol, see the papers by MacDougall (7) and MacDougall and Rehner (8). For the solutions listed in table 10 the values of γ and of γ_c do not differ appreciably from the corresponding values of f .

SUMMARY

This paper gives the solubility of silver acetate at 25°C. in 10, 20, and 30 per cent ethyl alcohol in the presence of the nitrates of potassium, sodium, lithium, calcium, strontium, and barium.

The Debye-Hückel equation seems to be valid for the solutions investigated up to values of the ionic strength listed in table 8.

Values of the mean ionic diameter are calculated for the solutions containing potassium nitrate or sodium nitrate.

Data are presented which will enable one to determine the activity coefficient of silver acetate in any of the solutions investigated.

The activity coefficient of silver acetate in solvents saturated with that salt but not containing any nitrate is given in table 10.

REFERENCES

- (1) ÅKERLÖF, G.: J. Am. Chem. Soc. **54**, 4125 (1932).
- (2) DEBYE AND HÜCKEL: Physik. Z. **24**, 185 (1923).
- (3) GOLDSCHMIDT, H.: Z. physik. Chem. **25**, 91 (1898).
- (4) HILL, A., AND SIMMONS, J.: J. Am. Chem. Soc. **31**, 821 (1909).
- (5) JAKES, A.: Trans. Faraday Soc. **5**, 225 (1909).
- (6) KNOX, J., AND WILL, H.: J. Chem. Soc. **115**, 853 (1919).
- (7) MACDOUGALL, F. H.: J. Am. Chem. Soc. **52**, 1390 (1930).
- (8) MACDOUGALL, F. H., AND REHNER, JOHN, JR.: J. Am. Chem. Soc. **56**, 368 (1934).
- (9) MURRAY: Standards and Tests for Reagent Chemicals. D. Van Nostrand Co., New York (1920).
- (10) RAUPENSTRAUCH, G. A.: Monatsh. **6**, 563 (1885).

THE PHYSICAL CHEMISTRY OF FLOTATION. VII

TRIMETHYLCETYLAMMONIUM BROMIDE AS A FLOTATION AGENT

IAN WILLIAM WARK

Department of Chemistry, University of Melbourne, Melbourne, Australia

Received January 30, 1936

Solutions of trimethylcetylammonium bromide possess, to an unusual extent, certain surface properties that influence the flotation of minerals. Films thin enough to exhibit beautiful interference colors may persist for weeks, and solutions can be used for such experiments with bubbles as are described by Boys (1). The compound is one of the best frothing agents known, even a 10 mg. per liter solution giving a very stable froth. The stability of the bubbles is not due to the formation of a thick semirigid film of the type produced by saponin, for, in dilute solutions, the substance does not seem to be present in colloidal form. From aqueous solutions the salt is adsorbed by a wide variety of minerals, and since it possesses the polar-nonpolar structure characteristic of collectors, it is almost a universal flotation reagent of the collector class. The angle of contact, determined as described in previous contributions (11, 9), is 60° for chalcopyrite and antimonite. This maximum angle has not been obtained for galena and pyrite, however, nor for the oxidized and silicate minerals. For these minerals the angle is usually within a few degrees of 50° .

It is of interest that silver bromide is not precipitated from solutions of the compound immediately upon the addition of silver nitrate, but upon boiling a precipitate slowly forms. For the work to be described the compound was purified by recrystallizing twice from alcohol and washing with ether.

TRIMETHYLCETYLAMMONIUM BROMIDE AS A COLLECTOR

Dilute solutions of trimethylcetylammonium bromide induce flotation of chalcopyrite, pyrite, sphalerite, galena, and other sulfide minerals. Several silicate minerals also respond to it, quartz, for example, responding to acid, neutral, and alkaline solutions, and rhodonite to neutral solutions. Tinstone responds to alkaline solutions, but calcite does not float in acid, neutral, or alkaline solutions. Captive bubble tests with polished mineral specimens confirm these observations. The compound modifies the surface of glass in such a way that an angle of contact of about 40° is obtained;

it is therefore impossible to keep glassware "clean" when in contact with dilute solutions.

Solutions of the compound possess a property that is unusual among collectors, a property moreover that is general for all the minerals floated by it. As the concentration is increased from 0 to about 50 mg. per liter, the floatability increases steadily. Further increases in concentration decrease the floatability, until somewhere below 500 mg. per liter, not a single particle floats. Meanwhile the frothing power of the solutions has steadily increased. Parallel results are obtained when polished mineral specimens are tested by a captive bubble of air, contact ceasing to be possible at a concentration of about 100 mg. per liter. The mechanism of the process preventing contact was suggested by tests with galena in a 50 mg. per liter solution. A newly formed bubble effected contact with the center of the galena surface, but a bubble thirty seconds old did not. Whatever the age of the bubble, contact could be effected with the sharp edges of the specimen, and when once established, the contact could be retained as the bubble was moved across the plane surface,—even to the central area with which contact could not be established with an aged bubble. The galena specimen, when transferred to pure water exhibited, for a time, an air avidity; this indicates that a film of the collector had been adsorbed. It is presumed that the galena was in a suitable condition for contact with air, but the surface of the bubble, as it aged, passed into a condition that hindered contact; nevertheless, the sharp edges of the galena could still rupture the bubble surface. In slightly more concentrated solutions, contact with the center could be established only by starting at an edge, while in a 500 mg. per liter solution contact at the edges could not be established.

These results were not unexpected. It has already been suggested (11) that the difficulty of rupturing an orientated adsorbed film of frother at the surface of a bubble would hinder its contact with a collector-conditioned mineral surface. But it is only when the film is particularly stable, as here, that its presence can be demonstrated by the bubble test. Support for this interpretation is given by a test in which a chalcopyrite specimen, previously conditioned by amyl xanthate, was placed in a 500 mg. per liter solution of trimethylcetylammonium bromide. Contact with air could not be effected, though the specimen, when replaced in water, still carried an air-avid film with the characteristic amyl xanthate contact angle.

Reagents of the type of trimethylcetylammonium bromide—that is, substituted ammonium salts and amines containing a large nonpolar group—may be of value for the flotation of silicate and other oxygen-bearing minerals. They possess the advantage over soap solutions that they do not form insoluble salts with such cations as calcium, copper, and

iron. Very low concentrations of the collector should suffice, since there would be no waste due to precipitation by cations derived from the ore or present in the water used.

DEPRESSANTS

Because a reagent is a depressant for a mineral when using a collector of the xanthate type, it does not follow that it will be a depressant also when using a nitrogenous collector. Thus 1 g. of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ per liter, which is much more than sufficient to prevent contact with the sulfide minerals in the presence of xanthates, does not prevent contact in the presence of 50 mg. per liter of trimethylcetylammonium bromide. Neither does it influence contact with or flotation of quartz. Similarly, a small concentration of sodium cyanide, though an excellent deactivator and depressant for

TABLE 1

Conditioned chalcopyrite in solutions of trimethylcetylammonium bromide

CONCENTRATION <i>mg. per liter</i>	CONTACT ANGLE	INDUCTION PERIOD ON PLANE SURFACE		DIRECT FLOTATION TESTS
		Extreme values	Mean value	
		<i>seconds</i>	<i>seconds</i>	
Nil	(54)	0.6 and 2.4	1.1	Slight film flotation
10	60	0.6 and 8.4	1.9	Excellent froth flotation
25	59	2.8 and 6.2	4.2	Excellent froth flotation
50	60	22 and 48	31	Good froth flotation
100	50*		>600	Fair froth flotation
500	Nil		>600	No flotation

* For this determination contact had first to be established with an edge.

sphalerite and pyrite respectively in xanthate flotation, is not a depressant with this reagent. The reagent causes flotation of so many minerals that its application in practice will depend upon the discovery of suitable depressants, which must be differential in their action. Depressants for some minerals have been found. Thus, galena is depressed by alkalis; in a solution containing 10 mg. per liter of the compound and 20 mg. per liter of lime, a partial separation of sphalerite from galena is possible. When the separation was attempted in a test tube, a little of the fine galena floated with the sphalerite. Copper sulfate and sodium cyanide when used together—but not singly—prevent the flotation of tinstone, sphalerite, and pyrite, but it has not been ascertained whether this action is differential between sphalerite and pyrite. Presumably the cupricyanide ion is the depressant. Acids and alkalis both prevent the flotation of rhodonite. In acid solutions quartz can be floated away from tinstone.

INDUCTION PERIOD FOR CONTACT BETWEEN AIR AND MINERAL

Some tests now to be described have a bearing on the explanation of the "induction period" for the establishment of contact. Sven-Nilsson (8) has observed that *true* contact (spreading) does not usually take place until some time after a bubble has come into *apparent* contact with a suitably conditioned mineral surface. The time that elapses before spreading commences, he terms the induction period. It increases with the size of the bubble, but the manner of its dependence upon other variables has not yet been established. Using a stopwatch, the induction period has been determined for a chalcopyrite specimen in a series of solutions of trimethylcetylammmonium bromide of different concentrations (see table 1). To ensure that the surface condition was as nearly as possible identical in all tests, the newly polished specimen was conditioned in a 500 mg. per liter solution and rinsed in water before it was placed in the

TABLE 2

Dependence of angle of contact at a submerged paraffin surface on concentration of trimethylcetylammmonium bromide

CONCENTRATION OF AMINE	ANGLE OF CONTACT	INDUCTION PERIOD
<i>mg. per liter</i>		
Nil	107, 106, 109°	Too small to be measured by a stopwatch
10	100	
25	94.5	
50	92	
100	80, 79	Up to 2 seconds
250	66	Very irregular
500	Nil	

test solution. Evidently the induction period is dependent upon the concentration of the compound. This is presumably because at high concentrations the adsorbed film is difficult to rupture.

CONTACT AT A PARAFFIN SURFACE

The condition of the surface of the bubble cannot account completely for the influence, recorded in table 2, of the concentration of trimethylcetylammmonium bromide on the angle of contact at the surface of paraffin wax. The wax was purified first by heating with a strong sulfuric acid solution and then with a strong caustic soda solution. The test surface was formed on a glass base by allowing molten wax to solidify in contact with the air; the hysteresis effect was almost absent because of the smoothness of this surface. Since the angle of contact changed slowly with time even in distilled water, the recorded angles were measured immediately after immersion of the wax in the solution.

Variations in the surface tension of the solution, no matter how large, could not account for a reduction in the angle to below 90° , since in the Young equation for the cosine of the contact angle, the surface tension occurs only as the sole term of the denominator and therefore changes in it could not alter the sign of the cosine of the angle of contact, as happens when the angle passes through 90° (10). The results prove that the surface energy at the paraffin-water interface has changed in such a way as to render the paraffin more water-avid or less air-avid. Such a change may be a chemiadsorption of the amine, with the paraffin wax attracting the alkyl groups of the substituted ammonium salt and the polar group orientated outwards, or it may be a kind of Gibbs' adsorption at this interface. If a film is formed, it can have no very strong binding forces, for on placing the paraffin in pure water the usual contact angle (107.5°) was obtained.

SURFACE TENSION MEASUREMENTS

Perhaps the best method of studying adsorption is to attempt to apply the Gibbs' equation to measurements of the change in surface tension of a solution with concentration. Most of the methods of measurement of surface tension are inapplicable if, as here, the solution forms a finite contact angle with glass. The "maximum bubble pressure" method, which is stated to be applicable when the contact angle is finite, was therefore adopted (7). It was found, however, that the finite contact angles that *dilute* solutions of trimethylcetylammonium bromide form with glass, though they may not directly influence the maximum bubble pressure, do prevent the apparatus from functioning smoothly. Consequently results could not be obtained for solutions of concentration lower than 50 mg. per liter.

There is an unexplained lack of agreement between the results of those who have measured surface tensions of aqueous solutions of surface-active compounds. The work of Harkins and Brown (4) suggests that insufficient attention has been paid to the time necessary for the establishment of the equilibrium or static value of surface tension. Schmidt and Steyer (6) claim that equilibrium is not immediately established even in pure water.

The surface tensions of solutions of trimethylcetylammonium bromide, measured by the bubble pressure method, vary with the time interval between the formation of successive bubbles in the manner shown in figure 1. For each strength of solution the measured surface tension approaches a steady minimum value as the rate of bubble formation is decreased. This steady value is presumably the static value corresponding to the attainment of an adsorption equilibrium. The dynamic value, i.e., the value corresponding to a surface concentration equal to the bulk

concentration, was not measured, but—whatever the concentration—it is evidently very much closer to, and may not differ greatly from, the value

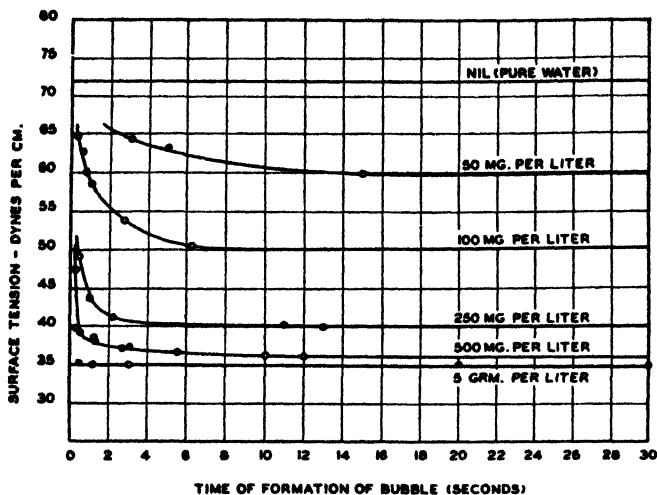


FIG. 1. Relationship between the value of the surface tension of solutions of trimethylcetyl ammonium bromide of various concentrations and the "age" of their surfaces. Temperature, $25 \pm 1^\circ\text{C}$.

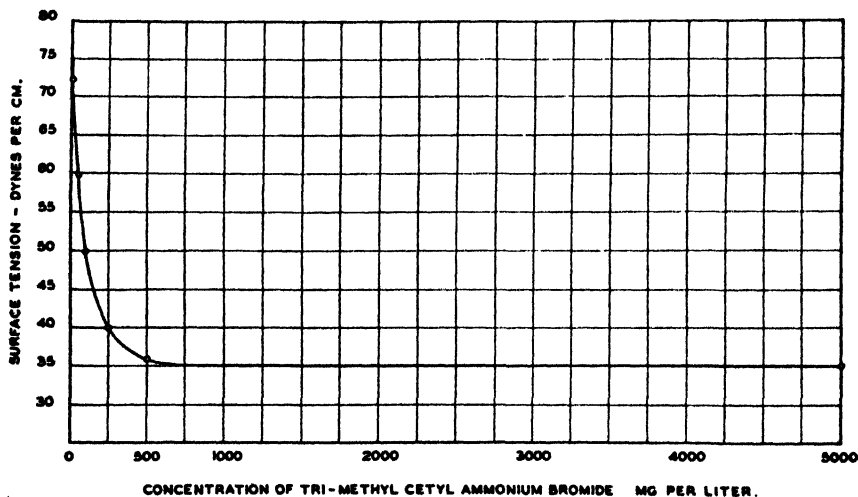


FIG. 2. Relationship between concentration of solutions of trimethylcetyl ammonium bromide and their static surface tensions. Temperature, $25 \pm 1^\circ\text{C}$.

for pure water. The indicated slow attainment of equilibrium is due to the slow diffusion to the surface of such a large molecule as trimethylcetyl ammonium bromide. It is evident, moreover, that equilibrium is

most rapidly established in the most concentrated solutions. This is because of the greater concentration of solute molecules that are available close to the surface for the formation of the adsorbed layer.

Figure 2, constructed from figure 1, shows the relationship between the concentration of trimethylcetylammonium bromide and the static surface tension. Up to a concentration of 1 g. per liter, the higher the concentration the lower is the static surface tension and, presumably, the more of the dissolved collector is adsorbed at the surface, but already in a 500 mg. per liter solution the surface must consist largely of orientated solute molecules. It is apparent that if the adsorbed layer around a bubble is a hindrance to contact with a suitably conditioned solid surface, contact will be most readily established in dilute solutions.

FROTHING

In figure 2 a condition has been reached at which an increase in concentration no longer lowers the surface tension. H. M. Cassel (2) in discussing a similar case, states that at a point of zero slope in the surface tension-concentration curve for sodium palmitate, the Gibbs' theorem indicates that no adsorption at all takes place. The application of the Gibbs' theorem is inadmissible, however, when complete, or almost complete orientated films of polar-nonpolar compounds are present. Langmuir (5) states that such films at the surface of aqueous solutions may possess the properties of liquids or solids.

Corresponding to the large difference between the static and dynamic values of the surface tension, even the stronger solutions froth strongly (compare Foulk (3)). This certainly indicates that there is an adsorption film at the interface, despite the horizontal nature of the concentration-surface tension curve beyond 1 g. per liter.

The writer gratefully acknowledges his indebtedness to the companies for which the work was carried out, namely, Broken Hill South Ltd., North Broken Hill Ltd., Zinc Corporation Ltd., Electrolytic Zinc Co. of Australasia Ltd., Mt. Lyell Mining & Railway Co. Ltd., and the Burma Corporation Ltd.; to Mr. H. Hey, under whose general direction the work was carried out; and to Professor E. J. Hartung for providing laboratory accommodation.

REFERENCES

- (1) BOYS: *Soap Bubbles*. London (1924).
- (2) CASSEL: *J. Am. Chem. Soc.* **57**, 2009 (1935).
- (3) FOULK: *Kolloid-Z.* **80**, 115 (1932).
- (4) HARKINS AND BROWN: *J. Am. Chem. Soc.* **41**, 499 (1919).
- (5) LANGMUIR: *Gen. Elec. Rev.* **38**, 402 (1935).
- (6) SCHMIDT AND STEYER: *Ann. Physik* **79**, 442 (1926).
- (7) SUGDEN: *The Parachor and Valency*. London (1930).

- (8) SVEN-NILSSON: Proc. Royal Swedish Inst. Eng. Research, No. 133 (1935);
Kolloid-Z. **69**, 230 (1934).
- (9) WARK, E. E., AND WARK, I. W.: J. Phys. Chem. **37**, 797 (1933).
- (10) WARK, I. W.: J. Phys. Chem. **37**, 623 (1933), see equation on p. 624.
- (11) WARK, I. W., AND COX, A. B.: Trans. Am. Inst. Mining Met. Engrs. **112**, 189
(1934).

THE REACTIVITY OF HALOGEN COMPOUNDS. II

THE RATES OF REACTION AND THE ENERGIES OF ACTIVATION OF 2,4-DINITROCHLOROBENZENE WITH AROMATIC PRIMARY AMINES

ATTAR SINGH AND D. H. PEACOCK

University College, Rangoon and Judson College, Rangoon, India

Received November 15, 1935

In earlier papers (8, 9) it was pointed out that a relation existed between constitution and energy of activation for the reaction between benzyl chloride and *m*- and *p*-toluidine and the corresponding dimethyltoluidines. The relation observed was that which would be expected on the Lapworth-Robinson hypothesis, assuming that reactivity in this reaction is helped by electron accession to, or availability at, the nitrogen atom of the amino group; the *p*-methyl group lowered the energy of activation as compared with the *m*-methyl group. The correspondence between the behavior of the tertiary bases, where only the addition reaction took place, and that of the primary bases was taken as evidence that the step which governed the rate of reaction for primary amines was also the addition reaction and not the reactivity of the hydrogen atom of the primary amino group. These conclusions are supported by the behavior of *m*- and *p*-nitrobenzyl chlorides with aromatic primary and tertiary bases (7, 10).

Further confirmation of the connection between constitution and energy of activation has been obtained by a study of the reaction between 2,4-dinitrochlorobenzene and certain aromatic primary amines. This reaction has been studied by Rheinlander (11) for aniline at one temperature and different concentrations, and by Van Optall (13) for a series of aromatic amines. In addition to the results at two temperatures given in table 2 Van Optall also measured the rate of reaction at one temperature of 2,4-dinitrochlorobenzene with the following: *o*-toluidine, *o*-, *m*-, *p*-chloroaniline, *o*-, *m*-, *p*-nitroaniline, *o*-anisidine, *o*-phenetidine, *p*-aminoacetophenone, *o*- and *p*-aminodiphenyl, α - and β -naphthylamine, and the secondary bases methylaniline and piperidine. We have determined the velocity of reaction in ethyl alcohol solution at two temperatures; from these results the value of the energy of activation, E , and the quantity $\log A$, in the equation $k = Ae^{-E/RT}$ have been determined. In table 1 are collected the results of our experiments.

The velocity constants given above represent in nearly every case the

mean of at least two independent experiments, but the energies of activation calculated from them cannot be regarded as accurate to within less than about 300 cal. The extreme error for a difference in energy of activation is therefore about 600 cal. The error of 300 cal. in the energy of activation would cause an error of rather less than 0.3 unit in the value of

TABLE 1

Velocity constants, energies of activation, and action constants for the reaction between 2,4-dinitrochlorobenzene and some primary aromatic amines in ethyl alcohol solution

[Dinitrochlorobenzene] = 0.1 M. Unit of time, minutes

BASE	CONCENTRATION	$10^4 k_m^\circ \text{C.}$	$10^4 k_{40}^\circ \text{C.}$	E (IN CALORIES)	LOG A
	M				
Aniline.....	0.4	6.91	12.3	11180	5.8
Aniline.....	0.8	6.49	11.8	11520	5.9
<i>o</i> -Toluidine.....	0.4	0.384	0.785	13860	6.4
<i>o</i> -Toluidine.....	0.8	0.333	0.725	15080	7.2
<i>m</i> -Toluidine.....	0.4	9.75	17.7	11560	6.2
<i>m</i> -Toluidine.....	0.8	8.76	16.8	12620	6.9
<i>p</i> -Toluidine.....	0.4	21.3	35.7	10060	5.4
<i>p</i> -Toluidine.....	0.8	19.0	33.2	10810	5.9
<i>o</i> -Chloroaniline.....	0.8	0.01 (approx.)			
<i>m</i> -Chloroaniline.....	0.4	0.44	0.86	13010	5.9
<i>m</i> -Chloroaniline.....	0.8	0.395	0.770	12940	5.8
<i>p</i> -Chloroaniline.....	0.4	1.49	2.81	12300	5.9
<i>p</i> -Chloroaniline.....	0.8	1.34	2.57	12620	6.1
<i>o</i> -Bromoaniline.....	0.8	0.01 (approx.)			
<i>m</i> -Bromoaniline.....	0.4	0.419	0.912	15080	7.3
<i>m</i> -Bromoaniline.....	0.8	0.374	0.842	15730	7.7
<i>p</i> -Bromoaniline.....	0.4	1.08	2.29	14570	7.4
<i>p</i> -Bromoaniline.....	0.8	0.975	2.11	14960	7.6
<i>o</i> -Anisidine.....	0.4	2.63	4.72	11330	5.5
<i>o</i> -Anisidine.....	0.8	2.17	4.40	13700	7.1
<i>m</i> -Anisidine.....	0.4	5.00	8.31	9850	4.7
<i>m</i> -Anisidine.....	0.8	3.99	6.98	10840	5.3
<i>p</i> -Anisidine.....	0.4	67.4	111.0	9670	5.7
<i>p</i> -Anisidine.....	0.8	58.1	98.6	10250	6.0
α -Naphthylamine.....	0.4	0.222 (?)	0.363	9530	
α -Naphthylamine.....	0.8	0.149	0.279	12160	
β -Naphthylamine.....	0.4	2.73	5.03	11850	
β -Naphthylamine.....	0.8		3.92		

log A and a maximum error of twice this amount in differences. This can be looked at in another way: if two reactions have the same value for A and if the ratio of the velocities is 2.7 or less, then the difference in E necessary to give this ratio is within the limits of experimental error. In such a case reliable evidence can only be obtained by a large number of determinations.

When meta-substituted derivatives are compared with para, it is seen that in every case the faster reaction has the lower energy of activation. For the reaction considered:

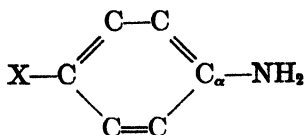
$$E_p - E_m = RT (\log_e A_p/A_m - \log_e k_p/k_m)$$

In tables 1 and 2 $E_p - E_m$ is always of the same sign as $\log_e k_m/k_p$. On the other hand the sign of $\log_e A_p/A_m$ varies, possibly through experimental error, and therefore the value of $\log_e k_m/k_p$ appears to be governed mainly by the changes in E . For these reactions, therefore, the change in energy of activation appears to be the chief factor in the alteration of the velocity constant. Secondly, the change in energy of activation is of the nature expected on the basis of the Lapworth-Robinson hypothesis. The argument for this need only be briefly reviewed, as it has already been dealt with elsewhere (1, 4, 5). The reactivity of these amines is determined by electron availability at the nitrogen atom of the amino group, and this in turn depends upon electron availability at, or accession to, the carbon atom

TABLE 2
Energies of activation calculated from the results of Van Optall (13)

NAME	10 ³ k _m , °C	k ₁₀₀	E (IN CALORIES)
Aniline	8 5	0.286	10360
<i>p</i> -Toluidine	21.2	0.7057	10330
<i>m</i> -Toluidine	10 9	0.4248	10800
<i>p</i> -Anisidine	81 9	0.6718	6200
<i>p</i> -Phenetidine	85 7	2.026	9320

to which it is attached; the greater the electron availability at this carbon atom, the greater the availability at the attached nitrogen atom. This can be looked at in another way. The dipole moment of aniline, its lower reactivity and basicity as compared with fatty amines, all suggest that the phenyl group is able to, and does, make a demand upon the two unshared electrons of the amino group, reducing their mobility. Increase of electron availability at the carbon atom to which the nitrogen atom is attached—i.e., reduction in the demand made by the phenyl group—increases the mobility of these unshared electrons of the nitrogen atom. This effect, relayed from the carbon atom to the nitrogen atom, would be expected to be less in the nitrogen atom than in the carbon atom from which it is relayed, as pointed out by Waters (14). Increased reactivity due to a sub-



stituent X would therefore be expected to be greater at C₄ than at the nitrogen atom. In other words, the reactivity of these amines would be expected to resemble that of the corresponding benzene derivatives towards electron-seeking reagents, but the differences would be less marked in the amines than in the originating benzene derivative.

It follows (1, 5) that a substituent which leads to increased electron availability at the para carbon atom, should lower the energy of activation of the amine in the para compound as compared with the meta, and raise the reaction velocity of the para compound as compared with the meta. Ortho-para directing substituents in the para-position in the amine should raise the reaction velocity and lower the energy of activation, as compared with the effect of the same substituent in the meta-position. Meta directing substituents should have the opposite effect. For reaction velocities these conclusions are supported by Van Optall's results and ours for the toluidines and chloroanilines, by Van Optall's for nitroanilines, and by our results for the bromoanilines and anisidine.

For the energies of activation the evidence is not so decisive. In every case, however, the difference between the energy of activation of the para compound and that of the meta compound is of the sign predicted by the Lapworth-Robinson hypothesis. In one case—the anisidines—the difference for both concentrations used is within the limits of experimental error. If the energies of activation for these meta and para compounds were really equal, then experimental error should give an equal number of values above and below equality. That all values for the meta compound are above those for the para—in many cases outside the range of experimental error—suggests that the meta compounds examined really have higher energies of activation than the para. The case of the anisidines is interesting. If the values of *A* were the same for the meta and the para compounds the difference in *E* required to produce the observed difference in velocity would be about 1400 cal., outside the range of experimental error. The observed differences are much smaller, and it may be that here the difference in reactivity is partially due to differences in *A*.

These results agree with those of Van Optall (13) in showing markedly the effect of para substituents. The order of reactivity is: OCH₃ > CH₃ > H > Cl > Br. The order is reversed for the energies of activation; the lower the energy of activation the greater the velocity of reaction. The effect on energy of activation is to a large extent that which would be expected from the Lapworth-Robinson hypothesis. The electron-repelling methyl group lowers the energy of activation. Chlorine and bromine have an inductive effect greater than their electromeric effect and both raise the energy of activation, bromine more than chlorine. Betti has also observed that bromine in some cases has a greater negative action than chlorine. The methoxyl group occupies a somewhat anomalous position which can

possibly be ascribed to its large electromeric effect, and which agrees with its marked ortho-para directive effect. Baker (1) has also observed high velocities for substances containing the methoxyl group in the para-position to the reacting group.

Nathan and Watson (6) and Williams and Hinshelwood (4) have shown that for several reactions the differences in the energies of activation of substituted benzene derivatives are nearly proportioned to the dipole moments of C_6H_5X . For the reaction between benzoyl chloride and aromatic amines of the type $XC_6H_4NH_2$, Williams and Hinshelwood took the mean molecular diameter as constant and used the approximate equation:—

$$k = \text{const.} \times (1/M)^{\frac{1}{2}} \times e^{-E/RT}$$

Whence:

$$2.303 \log kM^{\frac{1}{2}} = \text{const.} - E/RT$$

TABLE 3

Values of E , $\log kM^{\frac{1}{2}}$, μ C_6H_5X , and $\log A$ for para derivatives

BASE	E (IN CALORIES)	$10^3k_m^\circ C.$	$\log_{10} 10^3kM^{\frac{1}{2}}$	$\frac{\mu \times 10^{18}}{(C_6H_5X)}$	LOG A
<i>p</i> -Anisidine.....	9670	67 4	1.7706	-1 2	5 7227
<i>p</i> -Toluidine	10060	21 3	1 2510	+0.4	5 4994
Aniline.....	11180	6 91	0 7418	0	5 8085
<i>p</i> -Chloroaniline.....	12300	1.49	0 1199	-1.5	5 9402
<i>p</i> -Bromoaniline	14570	1 08	0 0177	-1.5	7 4234

and the differences in E were found to run parallel with the differences in $\log kM^{\frac{1}{2}}$. In table 3 are collected the values of E , calculated from the temperature coefficients, of $\log kM^{\frac{1}{2}}$, of μ , and of $\log A$.

From table 3 it is seen that, apart from *p*-anisidine, the results confirm the relationship established earlier (4, 6). *p*-Anisidine is anomalous in that it should have an energy of activation between that of aniline and chloroaniline to correspond with its dipole moment. The results of Van Optall (table 2) confirm this abnormality and show that it is true also of *p*-phenetidine.

For the meta compounds (see table 5) the order of velocity constants is $CH_3 > H > OCH_3 > Cl > Br$, and the order of energies of activation is $Br > Cl > CH_3 > H > OCH_3$. The electromeric effects are usually regarded as negligible in meta compounds, so that the effects here may be ascribed mainly to the inductive effect. Bromine and chlorine, electron-attracting groups, raise the energy of activation as would be expected. The methyl group should lower the value of E ; the slight rise may be due to a steric effect exerted from the meta-position. The methoxyl group

is again anomalous; it will be noticed that the group occupies its correct position in the order of velocity constants, and this case obviously needs further checking.

The effect of ortho substituents on the energy of activation has already been discussed (9) for the reaction between benzyl chloride and *o*-toluidine (cf. von Braun (2)). With dinitrochlorobenzene similar results were observed. The energy of activation for *o*-toluidine is markedly greater than that for the other toluidines and for aniline. The value of the action constant, although liable to experimental error, suggests that the probability of reaction is greater than for the para compound. The effect of the ortho substituent is thus not to hinder a reaction in a complex raised to the

TABLE 4

Energies of activation and dipole moments (Williams and Hinshelwood (4))

Reaction: benzoyl chloride and amine, $X \cdot C_6H_5NH_2$

X =	$100k_{\infty}^{\circ}C.$	E	$\mu \times 10^{18}$ C_6H_5X
H	6.88	7350	0
<i>p</i> -CH ₃	29.8	6800	+0.4
<i>p</i> -Cl	1.50	7600	-1.5
<i>p</i> -NO ₂	0.0042	11800	-3.9

TABLE 5

Energies of activation and values of $\log kM^{\frac{1}{2}}$ for meta compounds

BASE	$10^4k_{\infty}^{\circ}C.$	E	$\log_{10}10^4kM^{\frac{1}{2}}$	$\log A$
<i>m</i> -Anisidine.	5.00	9850	1.6409	4.7200
Aniline.	6.91	11180	1.7418	5.8085
<i>m</i> -Toluidine.	9.75	11560	1.9116	6.2320
<i>m</i> -Chloroaniline.	0.44	13010	0.5902	5.9195
<i>m</i> -Bromoaniline.	0.419	15080	0.6065	7.3697

activated state but to increase the energy of activation. The methyl group as an electron-repelling group ought to exert in the ortho-position an effect similar to that which it exerts in the para-position, that is, it should make easier the displacement necessary for activation, and when the methyl group is directly attached to the nitrogen atom as in monomethylaniline, then the rate of reaction with benzyl halides is faster than with aniline, although one might expect steric hindrance to operate here. The *o*-methyl group therefore exerts some special influence on the amino group, which may be exerted in two ways. It has already been suggested (9) that this influence is of the nature of a coördination similar to that suggested by Sidgwick for *o*-nitrophenol and similar compounds. More recently Sidgwick (12) has pointed out that hydrogen shows little tendency to coördinate

with nitrogen to form chelate rings, and the effect observed here may be, as he suggests for other cases, due to resonance. The effect of the methyl group is here exerted on the molecule containing it (cf. Von Braun(2)). There is another possibility, an intermolecular effect. The process of activation has been pictured by Eyring and Polanyi (3) as involving approach of two molecules, and consequent displacement of electrons and nuclei until the complex is brought to a state in which the reactive groups can be regarded as attached to either molecule indifferently and the complex may then rearrange itself to form the reaction products. The energy of activation is thus an energy barrier that has to be overcome. An ortho substituent group, irrespective of any dipole effect, will tend to hinder the close approach of another molecule, the two electron clouds will repel one another, and so tend to raise the energy of activation. *o*-Anisidine also has a high energy of activation.

Reference to table 1 shows that increase in concentration of the base lowers the velocity constant, raises the energy of activation, and increases the value of *A*. Rheinlander (11) found that increasing the concentration of aniline lowers the velocity constant of the reaction. The changes in *E* and *A* are for the most part within the limits of experimental error, but it is perhaps noteworthy that, with the exception of *m*-chloroaniline, they are in one sense.

The experiments were all carried out in absolute alcohol solution. The ethyl alcohol used was dried over quicklime for twenty-four hours, boiled under reflux with fresh quicklime for one hour, fractionally distilled, and the middle fraction used. The 2,4-dinitrochlorobenzene was crystallized from alcohol and melted at 51°C. The β -form, m.p. 43°C., was also obtained and gave the same values for the velocity constant. The bases, aniline, *o*-toluidine, *m*-toluidine, *m*-chloroaniline, *m*-bromoaniline, *o*-anisidine, and *m*-anisidine were purified by conversion to their acetyl compounds, whose melting points were as follows: after crystallization from water or aqueous alcohol acetanilide, 114°C.; acet-*o*-toluidide, 110°C.; acet-*m*-toluidide, 66°C.; acet-*o*-chloroanilide, 73°C.; acet-*m*-bromoanilide, 87°C.; acet-*o*-anisidide, 84°C.; acet-*m*-anisidide, 79°C. The acetyl derivatives were then hydrolyzed. The steam-distilled bases were dried and distilled under reduced pressure or at ordinary pressure for aniline and the toluidines. The solid bases were generally purified by crystallization from suitable solvents: *p*-toluidine, 44°C. (petroleum ether); *p*-chloroaniline, 70.5°C. (absolute alcohol); *p*-bromoaniline, 63°C. (absolute alcohol); *p*-anisidine, 57°C. (distilled under reduced pressure); β -naphthylamine, 111.5°C. (absolute alcohol).

Solutions of known strength of dinitrochlorobenzene and the base in absolute alcohol were prepared and brought to thermostat temperature. The calculated volumes of each solution were then mixed in a 50-cc. glass-

stoppered flask and the volume made up to 50 cc. with absolute alcohol at the thermostat temperature; the time of mixing was taken as zero time. From time to time 10 cc. of the reaction mixture was withdrawn and run into a separating funnel containing 10 cc. of standard silver nitrate solution, dilute nitric acid, and 30 cc. of benzene. The excess silver nitrate was titrated with standard ammonium sulfocyanide, as described by Rheinlander (11). In some cases the crystalline product made difficult the withdrawal of samples, and in these cases the reaction was carried out in test tubes into which was put 10 cc. of a solution of each reactant of the proper strength and the tube then sealed up. In the case of the anisidines the color of the solution interfered with the endpoint in the volumetric estimation, and the chlorine was therefore estimated gravimetrically. The

TABLE 6
Results of some typical experiments at 45°C.

REACTANTS	TIME IN MINUTES	NH ₄ CNS IN CC.	AgCl IN GRAMS	<i>x</i>	<i>A</i> /2 - <i>x</i>	<i>B</i> - <i>x</i>	<i>k</i> ₄₅ *c.
0.4 <i>M</i> aniline; 0.9950 <i>N</i> /10 AgNO ₃ ; 1.0230 <i>N</i> /20 NH ₄ CNS	74	13.95		0.0282	0.1718	0.0718	0.0121
	108	12.1		0.0376	0.1624	0.0624	0.0122
	140	10.7		0.0448	0.1552	0.0552	0.0122
	156	9.8		0.0494	0.1506	0.0506	0.0127
0.8 <i>M</i> <i>p</i> -chloroaniline; 1.0105 <i>N</i> /10 AgNO ₃ ; 1.0207 <i>N</i> /10 NH ₄ CNS	513	7.75		0.0615	0.3385	0.0385	0.00256
	699	5.60		0.0725	0.3275	0.0275	0.00260
	900	4.15		0.0799	0.3201	0.0201	0.00256
	1067	3.20		0.0847	0.3153	0.0153	0.00256
0.4 <i>M</i> <i>p</i> -anisidine	12.01*		0.0541	0.0378	0.1622	0.0622	0.111
	15.48		0.0652	0.0455	0.1545	0.0545	0.1095
	18.55		0.0725	0.0506	0.1494	0.0494	0.1095
	21.45		0.0797	0.0556	0.1444	0.0444	0.112

*12.01 means 12 minutes 1 second.

results of some typical experiments are given in table 6; in all cases the concentration of the 2,4-dinitrochlorobenzene was 0.1 *M*. The reaction is



hence if [base] = *A* and [2, 4-dinitrochlorobenzene] = *B*

$$\frac{dx}{dt} = k(A - 2x)(B - x)$$

whence

$$k = \frac{1}{2t} \frac{1}{A/2 - B} 2.303 \log_{10} \frac{A/2 - x}{B - x} \frac{B}{A/2}$$

The reaction was very sensitive to the purity of the bases used. The so-called pure, distilled aniline gave a distinctly higher velocity constant than that given by the base prepared from the pure acetyl compound. The best commercial *o*-toluidine gave interesting results; the velocity constant fell off during the progress of the reaction. When the base was purified through the acetyl compound, a much lower initial value of the velocity constant was obtained and no falling-off during the reaction was observed, indicating that the commercial product contained a small amount of a more rapidly reacting impurity. This reaction may, therefore, be used as a test of the purity of aromatic amines. β -Naphthylamine was too sparingly soluble in alcohol at 35°C. for results to be obtained at 0.8 *M* concentration. The figure for α -naphthylamine at 0.4 *M* and 35°C. is only approximate. Dinitrochlorobenzene had no action on ethyl alcohol under the conditions of these experiments.

SUMMARY

1. The velocity of reaction of 2,4-dinitrochlorobenzene at 35°C. and 45°C. with the following bases at 0.4 and 0.8 *M* concentration has been found: aniline, *o*-, *m*-, and *p*-toluidine, *m*- and *p*-chloroaniline, *m*- and *p*-bromoaniline, *o*-, *m*-, and *p*-anisidine, and α - and β -naphthylamine.

2. The energies of activation for these reactions have been calculated.

3. The effect on the energy of activation of transferring a substituent from the meta- to the para-position is that predicted by the Lapworth-Robinson hypothesis.

4. The changes in energy of activation for the meta and para compounds have been compared with the dipole moments; the position of *p*-anisidine is anomalous. In the meta series both *m*-toluidine and *m*-anisidine occupy anomalous positions.

5. The low rate of reaction of *o*-toluidine seems due to a high energy of activation. The steric effect is thus an energy barrier.

6. In general, energy of activation seems the chief factor in determining velocity of reaction, but the reaction probabilities are not constant and the results are not decisive.

We thank the University of Rangoon for a grant towards the cost of this investigation, which is being continued.

REFERENCES

- (1) BAKER: J. Chem. Soc. **1933**, 1128.
- (2) VON BRAUN: Ber. **49**, 1101 (1916).
- (3) EYRING AND POLANYI: Z. physik. Chem. **12B**, 279 (1931).
- (4) HINSHELWOOD AND WILLIAMS: J. Chem. Soc. **1934**, 1079.
- (5) INGOLD AND SHAW: J. Chem. Soc. **1927**, 2918.
- (6) NATHAN AND WATSON: J. Chem. Soc. **1933**, 890, 1248.

- (7) PEACOCK: J. Chem. Soc. **127**, 2177 (1925).
- (8) PEACOCK: J. Phys. Chem. **31**, 535 (1927).
- (9) PEACOCK: Nature **129**, 57 (1932).
- (10) PEACOCK: J. Phys. Chem. **30**, 673 (1926).
- (11) RHEINLANDER: J. Chem. Soc. **123**, 3099 (1923).
- (12) SIDGWICK: Annual Reports **31**, 53 (1934).
- (13) VAN OPTALL: Rec. trav. chim. **52**, 901 (1933).
- (14) WATERS: J. Chem. Soc. **1933**, 1551.

STUDIES ON MOLECULAR WEIGHT CHANGES OF SULFUR MONOCHLORIDE¹

W. A. PATRICK AND N. HACKERMAN

Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland

Received January 25, 1936

The following investigation was undertaken with a view to studying the anomalous behavior of sulfur monochloride in connection with its boiling-point elevation as contrasted with its depression of the freezing point.

Raoult (13), near the end of the last century, measured the freezing-point lowering of glacial acetic acid and of benzene due to the addition of sulfur monochloride. The molecular weight of the monochloride as calculated from these data was 135, which corresponds to the formula S_2Cl_2 . This value agrees with those Dumas (9) and Marchand (9) found independently by vapor density measurements. Beckmann and Geib (3) and Beckmann and Junker (4) obtained similar results by the cryoscopic method, using a number of low-boiling solvents, e.g., ethyl chloride, sulfur dioxide, and phosgene.

The earliest mention of an investigation by a boiling-point method came in 1899. Oddo and Serra (12), using the Beckmann boiling-point apparatus, found the molecular weight of sulfur monochloride in benzene and carbon tetrachloride to be abnormal, i.e., 190 and 173, respectively. Two years later, however, Oddo (11) repeated the work more carefully and at the same time used a more rigorous method of calculation. This time he found the molecular weight in the same two solvents to be about 150, showing therefore no effect due to the solvent. However, he did find a slight increase in this value with increase in concentration.

From that time on the system sulfur-chlorine has been studied in more or less detail, but it was not until recently that more work was done on the molecular weight of sulfur monochloride in solution. Jones (6), by an ebullioscopic method, obtained a value in excess of 160 for the molecular weight of sulfur monochloride in carbon tetrachloride. His experiments also indicate that there is actually an effect due to the nature of the solvent. These results when taken in conjunction with those of Oddo indi-

¹Based on a dissertation submitted June, 1935, to the Board of University Studies of the Johns Hopkins University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

cate strongly that there is an inconstancy in the molecular composition of sulfur monochloride.

In view of the volatility of sulfur monochloride, with the resultant uncertainty in the composition of the solutions, it became necessary to limit the investigation to very dilute solutions. This limitation was advantageous from two standpoints. In the first place, change in the composition of the solution during ebullition was made negligible, and in the second place, no reasonable doubt could be entertained in regard to the application of Raoult's law.

Raoult's law may be applied in the following form if we take the vapor pressure of the solution at the boiling point to be equal to the sum of the partial pressures of the two components,

$$[760 + (dP_A/dT_A) \Delta T]x_A + [P_B^0 + (dP_B/dT_B) \Delta T]x_B = 760$$

The second term on the left is the correction due to the volatility of the solute, where P_B^0 is the vapor pressure of the solute at the boiling point of the solution and dP_B/dT_B is the slope of the vapor pressure curve at that temperature. When the solute is non-volatile both of these terms equal zero and the familiar relationship $\Delta T = Bx_B$ remains.

EXPERIMENTAL

Materials

In order to get some information on the effect of temperature, solvents with boiling points as far apart as possible were used. Because of the reactivity of the sulfur monochloride, it was rather difficult to obtain a large number of inert solvents. The liquids finally used were benzene, carbon tetrachloride, chloroform, cyclohexane, and toluene.

Benzene that had been purified by the method described by Greer (5) was available. Since it was known to be free of thiophene and carbon disulfide it was used without further treatment. Baker's c.p. carbon tetrachloride was distilled on the 11-foot, modified Podbielniak still described by Zinc (14). The fraction which had the value for n_D^{25} of 1.4575 was used. The cyclohexane was of Kahlbaum's "reagent" grade, and it was deemed unnecessary to purify it further. Baker's c.p. chloroform, which contains 0.5 per cent of alcohol, was treated in the following manner. Several hundred cubic centimeters of the chloroform was refluxed with 1 to 2 per cent of sulfur monochloride for about thirty hours. The resulting solution was washed several times with a solution of pure sodium hydroxide and finally with distilled water. The chloroform was stored over calcium chloride for several days, and was then distilled in a closed system. Baker's c.p. toluene was treated in the same manner as that described for chloroform.

Merck's "technical grade" sulfur monochloride was distilled from 1 per cent of sulfur and 1 per cent of activated charcoal in the manner indicated by Mann, Vernon, and Pope (8). The final distillation was made in an all-glass still, using a 3-foot refluxing column filled with glass beads. In order to prevent contact with the air on transferring the sulfur monochloride from the receiver to the flask which was to hold it, the still was filled with dried nitrogen. The nitrogen was run through a three-way stopcock placed just in front of the pump. The sulfur monochloride was kept in a glass-stoppered Erlenmeyer flask from which the air had been displaced by dried nitrogen. The flask was then placed in a desiccator over calcium chloride.

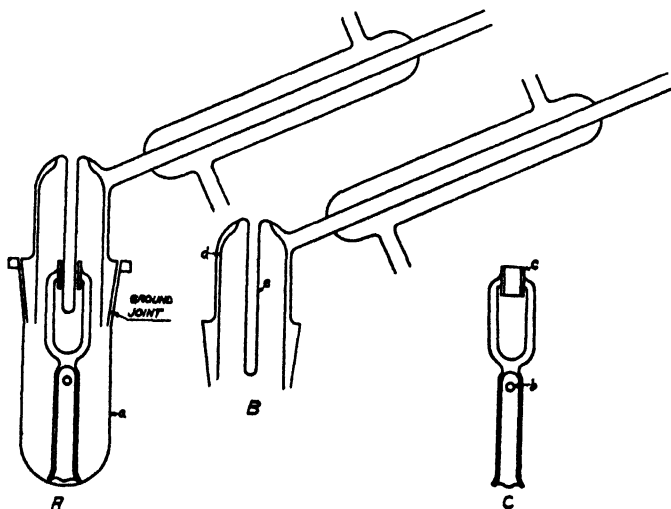


FIG. 1. The ebullioscope

Apparatus

Many types of ebullioscope are described in the literature, but it was thought best to design one modelled along the lines of the original Cottrell flask, which would be best adapted to the present purposes. The flask, consisting of three parts, is shown in figure 1. The lower body, A, is merely a piece of glass tubing 4.5 cm. in diameter, closed off at one end and ground at the other as the female of a ground-glass joint. The upper body, B, carries, besides the male of the ground joint, a shield and thermocouple well sealed into the top by a double ring seal. A condenser is sealed into the top on the outside at an angle of about 50°. The pump, C, is of a type used by Mair (7), the main difference being in the use of shorter arms and the absence of the heating element which he has sealed in the bottom.

The pump is flared at the bottom to cover a wider area which was a consequence of the use of external heating. Two identical flasks, one containing pure solvent and the other the solution, were used side by side in all the experiments in order to overcome the effects due to the fluctuation of the atmospheric pressure.

Because of the corrosive character of sulfur monochloride it was impossible to use the more efficient method of internal heating. The heat was supplied from the outside by two small, identical, electric heaters. The cores of the ovens were copper rods, shaped as tacks with concave heads. These were wound with 6 feet of No. 24 B & S nichrome wire, each oven having a resistance of 16.6 ohms. The ovens were connected in series with each other, so that voltage changes in the line would affect both similarly. A variable resistance was also placed in the heating circuit, in series, to control the current input.

A differential method of measuring the boiling-point rise, which is fully described by Jones (6) and Zinc (14), was used. It consisted merely of a galvanometer used as a deflection instrument and a simple two-junction thermocouple. The thermocouple consisted of No. 36 B & S double silk-covered copper wire and No. 30 B & S double silk-covered constantan, both of which were obtained from the Driver, Harris Co.

Procedure

The apparatus was calibrated by measuring the difference in temperature between boiling carbon tetrachloride and a solution of naphthalene in carbon tetrachloride of known composition. Baker's c.p. naphthalene, which contains only 0.002 per cent of non-volatile matter, was sublimed three times before being used in the calibration.

The actual measurements were made by first obtaining the galvanometer reading with no current flowing, merely as a reference point. Then with pure solvent boiling in each flask an initial reading was taken. After the flasks had cooled sufficiently the one which was to contain the solution was opened and a weighed amount of sulfur monochloride added. During the introduction of the solute a slow stream of dried nitrogen flowed through the flask continuously. The flask was then closed and both vessels were connected by pieces of rubber tubing, from the end of their condensers, to a large copper box containing calcium chloride. The box was open, at the far end, to the air. The heating current was started again, and after the liquid in both flasks was boiling evenly another reading was taken. The difference in the two positions on the scale gave the boiling-point rise directly. Several additions of solute were made in each experiment until the galvanometer mirror had swung over almost the whole scale.

TABLE 1
Sulfur monochloride and benzene (see figure 2)

x	W	x	W
0 02005	140.0	0.01240	136.6
0.03733	148.5	0.02470	143.6
0 04674	152.4	0 03704	148.4
0.05057	152.5	0.04653	153.7
0.06617	155.3	0 05945	153.9
		0 06645	154.4
+ (in figure 2) represents values of x and W obtained February 27, 1935		● (in figure 2) represents values of x and W obtained March 21, 1935	

TABLE 2
Sulfur monochloride and cyclohexane (see figure 3)

x	W	x	W	x	W
0.00491	149.5	0.01376	152.9	0 01694	155.2
0 02265	153.7	0 02640	158.2	0 03465	161.2
0 03697	160.2	0.04335	165.7	0 04715	167.6
0 04933	165.6	0 05078	167.8	0 05670	168.1
0 05946	168.7	0 06126	168.8	0.06840	172.2
0 06501	169.5				
○ (in figure 3) represents values of x and W obtained March 4, 1935		+ (in figure 3) represents values of x and W obtained March 6, 1935		● (in figure 3) represents values of x and W obtained March 15, 1935	

TABLE 3
Sulfur monochloride and chloroform (see figure 4)

x	W	x	W
0 00824	193.4	0 00943	187.9
0 02332	167.2	0 02156	169.0
0 03373	165.8	0 02992	166.2
0 04540	163.9	0.04050	164.7
0 05386	164.4	0 05685	165.4
○ (in figure 4) represents values of x and W obtained March 13, 1935		+ (in figure 4) represents values of x and W obtained March 14, 1935	

RESULTS

Calibrations were made at various intervals throughout the series of experiments and an average of all the values was obtained. Using 31.9

TABLE 4
Sulfur monochloride and toluene (see figure 5)

x	W	x	W
0.01542	89.4	0.01857	94.6
0.02902	102.5	0.04707	111.7
0.04851	107.1	0.06499	112.9
0.06338	112.6	0.08621	105.0
0.07340	113.5	0.11006	101.9
0.09235	109.6		
0.11277	99.8		

○ (in figure 5) represents values of x and W obtained March 27, 1935

+ (in figure 5) represents values of x and W obtained March 29, 1935

TABLE 5
Sulfur monochloride and carbon tetrachloride (see figure 6)

x	W	x	W	x	W	x	W
0.01749	143.5	0.01519	146.8	0.01438	157.1	0.01618	183.6
0.02817	147.2	0.02345	151.4	0.02425	159.7	0.02599	182.1
0.04545	153.9	0.03649	157.4	0.03538	170.2	0.03551	180.9
0.05643	156.8	0.04730	162.6	0.04677	169.9	0.04350	180.8
0.06334	158.0	0.05715	166.2	0.05989	172.5	0.05013	182.0
						0.06099	183.0

Values obtained February 20, 1935 Values obtained March 1, 1935 Values obtained March 12, 1935 Values obtained April 8, 1935

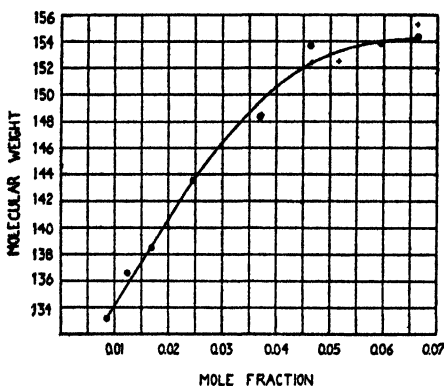


FIG. 2

FIG. 2. Sulfur monochloride and benzene. ○, February 22, 1935; +, February 27, 1935; ●, March 21, 1935

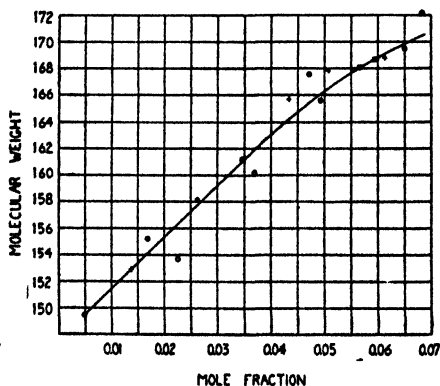


FIG. 3

FIG. 3. Sulfur monochloride and cyclohexane. ○, March 4, 1935; +, March 6, 1935; ●, March 15, 1935

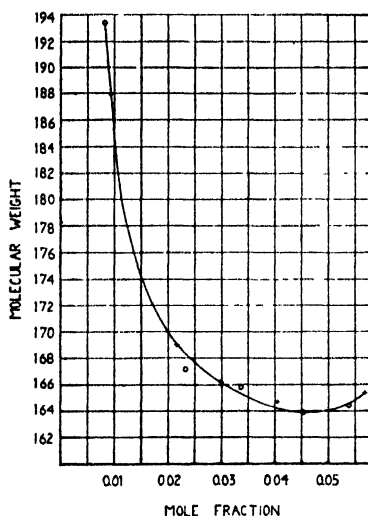


FIG. 4

FIG. 4. Sulfur monochloride and chloroform. O, March 13, 1935; +, March 14, 1935

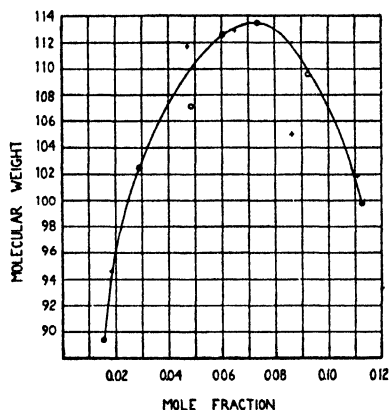


FIG. 5

FIG. 5. Sulfur monochloride and toluene. O, March 27, 1935; +, March 29, 1935

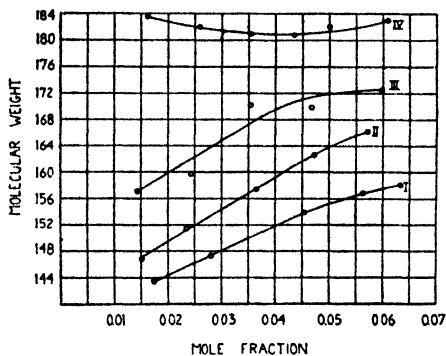


FIG. 6

FIG. 6. Sulfur monochloride and carbon tetrachloride. I, February 20, 1935, II, March 1, 1935; III, March 12, 1935; IV, April 8, 1935

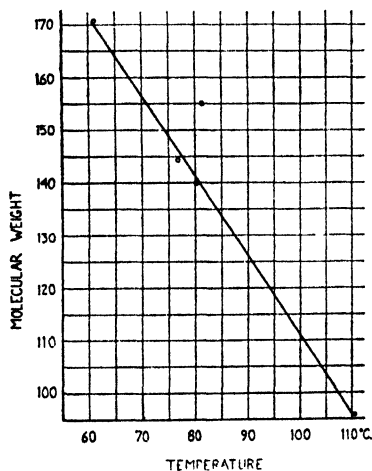


FIG. 7

FIG. 7. Effect of temperature on the molecular weight of sulfur monochloride

as the boiling-point constant, it was found that each division was equivalent to 0.0393°C .

In tables 1 to 5 x is the mole fraction of the solute and W is the molecular weight calculated from the boiling-point rise. Two or more series of

measurements were made with each solvent in order to afford a check. The values of all the experiments in the same solvent are plotted on a single curve.

In the experiments listed the age of the sulfur monochloride was about the same with each measurement in any one solvent and at no time was it more than fifteen days old. In table 5 is listed an experiment in which sulfur monochloride which had been distilled on February 19, 1935 was used throughout.

One observation may be noted here in connection with the experiments in toluene. As the measurement progressed, the solution which had had the normal golden-yellow color of sulfur monochloride during the first hour of boiling, became gradually darker until at the conclusion of the experiment the liquid was a very definite pink. There was no indication of a color change in any of the other solutions.

DISCUSSION

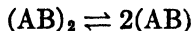
We are forced to the conclusion that the molecular weight of sulfur monochloride exhibits a rather puzzling series of changes. It is obviously necessary to consider the method of preparation and the age of the compound, as well as the concentration and temperature of the solution in which the molecular weight is being determined. It might be well to mention here that the toluene experiments do not properly form a part of this study, since it is obvious that the high temperatures brought about the formation of sulfur dichloride, as evidenced by the pink color of the solutions. This causes complications of a nature which the data at hand are inadequate in solving. Moreover, the region past the maximum in figure 5 is somewhat outside the realm of dilute solutions and Raoult's law cannot be justly expected to apply.

Two simple conclusions may be drawn from the remaining experiments. First, we are dealing with a polymerized molecule which dissociates at higher temperatures. Figure 7 shows the molecular weight of sulfur monochloride, when x is approximately 0.02 in the various solvents, plotted as ordinate against the boiling point of the solvent as abscissa. Although the cyclohexane value is not in very good agreement, the effect of temperature is still unmistakable.

Second, the carbon tetrachloride experiments indicate that a progressive polymerization is taking place in the pure sulfur monochloride. From these results it would appear that the real equilibrium is not being measured in the boiling liquids, but that the true equilibrium rests on the side of the polymerized molecule (note the carbon tetrachloride experiment of April 8, 1935). It then becomes necessary to discover the cause of the sluggishness and the anomalous behavior of the reaction.

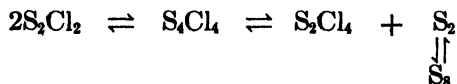
Furthermore the conditions of age and temperature are insufficient in

explaining all of the facts. For example, when using chloroform as the solvent we find that the molecular weight increases with dilution. Such behavior is hardly consistent with the law of mass action. If



dilution will certainly cause an increase in the right-hand member.

In the chloroform experiments one finds the molecular weight approaching 200 in the most dilute solutions and falling to 164 at a mole fraction of 0.044. A double molecule of sulfur monochloride should exhibit a molecular weight of 270, but such a condition should result in an increase in molecular weight with increasing concentration. The following assumption, however, offers some interesting possibilities:



We have here a series of changes whereby sulfur monochloride breaks up to form S_2Cl_4 and S_8 . From one mole of sulfur monochloride there would be formed $\alpha/8$ moles of S_8 and $\alpha/2$ moles of S_2Cl_4 , where α is the fraction transformed. The total number of moles at equilibrium would be

$$1 - \alpha + \alpha/2 + \alpha/8 = 1 - 3\alpha/8$$

If $\alpha = 1$ the molecular weight is 216, and if $\alpha = 0$ it is 135. By such a mechanism it is possible to account for a variation in molecular weights from 135 to 216, which is approximately the range covered in the experiments.

The effect of concentration before the final stage of equilibrium is reached is probably best explained by the effect of the solvent and temperature on sulfur itself. If we assume a reaction such as that just above we are permitted to postulate a great many forms of sulfur. Mellor (10) cites examples of the many different forms of sulfur existing in various solvents and at different temperatures. Furthermore the presence of the sulfur monochloride may alter the form of the sulfur markedly. Aten (2), for example, reported that in a solution of sulfur in sulfur monochloride there existed a ternary mixture of S_2Cl_2 , S_8 , and what he called S_r . In a previous paper (1) he showed that the molecule S_8 is S_8 and that of S_r is S_4 . The latter form alone may be sufficient to explain the apparent change in molecular weight with concentration, but if it is not adequate, certainly with all the possible ramifications of sulfur there may well exist, to some extent at least, the molecule S_2 . In this connection it is important to remember that the nature of the solvent may be profoundly altered by the presence of the sulfur monochloride.

SUMMARY

1. A modified Cottrell ebullioscope has been described.
2. The molecular weight of sulfur monochloride has been measured in various inert solvents at different concentrations.
3. It has been shown that the molecular weight of the sulfur monochloride seems to be affected by its age, the temperature, the nature of the solvent, and the concentration.
4. It has been postulated that the abnormal molecular weight is due to the presence of a polymer $(S_2Cl_2)_n$, which breaks up into S_8 and S_2Cl_4 ; also that the change in weight with concentration is due to an equilibrium between large and small molecules of sulfur.

REFERENCES

- (1) ATEN: Z. physik. Chem. **88**, 321-79 (1914).
- (2) ATEN: Verhandel. Akad. Wetenschappen Amsterdam **26**, 813-9 (1918).
- (3) BECKMANN AND GEIB: Z. anorg. Chem. **51**, 96 (1906).
- (4) BECKMANN AND JUNKER: Z. anorg. Chem. **55**, 371 (1907).
- (5) GREER: J. Am. Chem. Soc. **52**, 4191 (1930).
- (6) JONES, H. R.: Dissertation, The Johns Hopkins University, 1934.
- (7) MAIR: Bur. Standards J. Research **14**, 345 (1935).
- (8) MANN, VERNON, AND POPE: J. Chem. Soc. **119**, 634 (1921).
- (9) Cf. MELLOR: Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. X, p. 635. Longmans, Green and Co., New York and London (1930).
- (10) Reference 9, p. 23.
- (11) ODDO: Gazz. chim. ital. **31**, II, 222 (1901).
- (12) ODDO AND SERRA: Gazz. chim. ital. **29**, II, 318 (1899).
- (13) RAOULT: Cf. reference 12, p. 327.
- (14) ZINC: Dissertation, The Johns Hopkins University, 1934.

FERRIC SULFATE IN AQUEOUS SOLUTIONS OF OTHER SULFATES

F. K. CAMERON

Department of Chemistry, University of North Carolina, Chapel Hill, N. C.

Received December 9, 1935

INTRODUCTION

Ferric sulfate, $\text{Fe}_2(\text{SO}_4)_3$, with aqueous hydrogen sulfate forms a three-component system, but it is only in high concentrations of the acid that ferric sulfate is truly a component. At lower concentrations it is hydrolyzed, and the stable solid in contact with the liquid is either a basic sulfate or a solid solution of basic character. Furthermore, at ordinary temperatures no ferric sulfate of definite composition can exist as stable solid in contact with an aqueous solution unless the ratio of SO_3 to Fe_2O_3 be greater in the liquid phase than in the solid (1). Consequently, it would be expected that the addition of ferric sulfate to the aqueous solution of another sulfate must necessarily produce a four-component system.

However, alums, pseudo alums, and other double salts have been reported as crystallizing from clear solutions. Similar observations have been made on analogous aluminum compounds. The crystallization of ordinary potassium or ammonium alum is commonplace. Dobbins and his coworkers have shown in this laboratory that sodium alum is stable over wide ranges of concentration and a fairly wide range of temperature (2). Occleshaw has reported the pseudo alum $\text{FeSO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ related to the mineral halotrichite (3); the manganese compound $\text{MnSO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ and others are known. The possibility exists, therefore, under some conditions of temperature and concentration, of considering an aqueous solution of ferric sulfate and another sulfate as a three-component system.

From preliminary experiments it appeared difficult to obtain solutions from which *some* indefinite ferruginous material would not precipitate. It was attempted to add sufficient excess of sulfuric acid to prevent the indefinite solid from precipitating and to maintain a constant ratio between the excess acid and water. This latter condition was impracticable of complete realization. But the indefinite ferruginous material being apparently but slightly soluble, it was decided to ignore it with the slight

TABLE 1

Ferric sulfate in aqueous solutions of other sulfates at 25°C.

LIQUID PHASE			RESIDUE			SOLID PHASE
(NH ₄) ₂ SO ₄	Fe ₂ (SO ₄) ₃	Excess SO ₄	(NH ₄) ₂ SO ₄	Fe ₂ (SO ₄) ₃	Excess SO ₄	
per cent	per cent	per cent	per cent	per cent	per cent	
1.4	44.5	+0.7				?
1.5	44.2	+1.1				?
1.7	44.4	+2.3				(NH ₄) ₂ SO ₄ ·Fe ₂ (SO ₄) ₃ ·24H ₂ O and indefinite mixture
1.9	43.1	0.98	0.7	41.9	0.7	(NH ₄) ₂ SO ₄ ·Fe ₂ (SO ₄) ₃ ·24H ₂ O
2.2	39.2					(NH ₄) ₂ SO ₄ ·Fe ₂ (SO ₄) ₃ ·24H ₂ O
3.3	32.8					(NH ₄) ₂ SO ₄ ·Fe ₂ (SO ₄) ₃ ·24H ₂ O
4.8	28.7					(NH ₄) ₂ SO ₄ ·Fe ₂ (SO ₄) ₃ ·24H ₂ O
11.7	20.6	0.9	14.0	40.9	0.9	(NH ₄) ₂ SO ₄ ·Fe ₂ (SO ₄) ₃ ·24H ₂ O
14.8	18.0		14.2	41.1		(NH ₄) ₂ SO ₄ ·Fe ₂ (SO ₄) ₃ ·24H ₂ O
17.3	16.3	2.5				(NH ₄) ₂ SO ₄ ·Fe ₂ (SO ₄) ₃ ·24H ₂ O and (NH ₄) ₂ SO ₄
26.6	9.0					(NH ₄) ₂ SO ₄
40.8	1.4					(NH ₄) ₂ SO ₄
44.2	0.5	0.8				(NH ₄) ₂ SO ₄
K ₂ SO ₄	Fe ₂ (SO ₄) ₃	Excess SO ₄	K ₂ SO ₄	Fe ₂ (SO ₄) ₃	Excess SO ₄	
per cent	per cent	per cent	per cent	per cent	per cent	
2.83	27.8	0.4	28.8	37.3	4.4	2K ₂ SO ₄ ·Fe ₂ (SO ₄) ₃ ·14H ₂ O
2.94	24.3	0.7	29.8	35.6	4.3	2K ₂ SO ₄ ·Fe ₂ (SO ₄) ₃ ·14H ₂ O
3.34*	21.8	2.8	29.6	36.6	3.8	2K ₂ SO ₄ ·Fe ₂ (SO ₄) ₃ ·14H ₂ O
3.38	20.8	0.9	29.8	36.0	4.2	2K ₂ SO ₄ ·Fe ₂ (SO ₄) ₃ ·14H ₂ O
4.56	13.1	1.7				2K ₂ SO ₄ ·Fe ₂ (SO ₄) ₃ ·14H ₂ O
5.43	11.2	1.4				2K ₂ SO ₄ ·Fe ₂ (SO ₄) ₃ ·14H ₂ O
5.32	9.02	1.9	30.5	33.3	3.9	2K ₂ SO ₄ ·Fe ₂ (SO ₄) ₃ ·14H ₂ O
6.21	6.04	2.1	29.4	32.3	3.6	2K ₂ SO ₄ ·Fe ₂ (SO ₄) ₃ ·14H ₂ O
8.0	2.35	1.58				2K ₂ SO ₄ ·Fe ₂ (SO ₄) ₃ ·14H ₂ O
11.7	0.85	0.59				2K ₂ SO ₄ ·Fe ₂ (SO ₄) ₃ ·14H ₂ O and K ₂ SO ₄
11.9	0.69	0.68				K ₂ SO ₄
11.8	0.31	0.55				K ₂ SO ₄
11.5	0.10	0.26				K ₂ SO ₄
11.3	0.02	0.11				K ₂ SO ₄
12.2†	1.25	1.27				2K ₂ SO ₄ ·Fe ₂ (SO ₄) ₃ ·14H ₂ O and K ₂ SO ₄
12.0†	1.28	1.41				2K ₂ SO ₄ ·Fe ₂ (SO ₄) ₃ ·14H ₂ O and K ₂ SO ₄
12.5†	1.53	1.86				2K ₂ SO ₄ ·Fe ₂ (SO ₄) ₃ ·14H ₂ O and K ₂ SO ₄
13.1†	1.68	2.24				2K ₂ SO ₄ ·Fe ₂ (SO ₄) ₃ ·14H ₂ O and K ₂ SO ₄
13.7†	1.88	2.7				2K ₂ SO ₄ ·Fe ₂ (SO ₄) ₃ ·14H ₂ O and K ₂ SO ₄

TABLE 1—*Concluded*

LIQUID PHASE			RESIDUE			SOLID PHASE
FeSO ₄	Fe ₂ (SO ₄) ₃	Excess SO ₄	FeSO ₄	Fe ₂ (SO ₄) ₃	Excess SO ₄	
per cent	per cent	per cent	per cent	per cent	per cent	
0.38	44.75	1.48	0.04	48.14	-4.43	Basic ferric sulfate
0.82	44.15	1.93	0.05	48.51	-4.09	Basic ferric sulfate
1.36	43.79	3.19	0.08	47.40	-4.08	Basic ferric sulfate
2.01	43.32	2.98				Basic ferric sulfate
2.53	42.25	2.47	1.63	44.74	-4.44	Basic ferric sulfate
2.61	43.25	1.12				Basic ferric sulfate
3.07†	42.60	1.56	4.10	44.25	-4.05	FeSO ₄ ·7H ₂ O and a basic ferric sulfate
3.26†	41.71	1.99	7.90	40.10	-2.99	FeSO ₄ ·7H ₂ O and a basic ferric sulfate
4.90†	39.80	2.86	10.36	41.54	-3.95	FeSO ₄ ·7H ₂ O and a basic ferric sulfate
5.30†	38.42	3.61	6.91	43.41	-4.47	FeSO ₄ ·7H ₂ O and a basic ferric sulfate
8.16	36.60	1.90				FeSO ₄ ·7H ₂ O and ferric sulfate
10.47	28.36	0.25	49.89	6.26	-0.55	FeSO ₄ ·7H ₂ O
11.29	23.38	1.16				FeSO ₄ ·7H ₂ O
15.23	16.64	0.04	53.15	2.86	0.45	FeSO ₄ ·7H ₂ O
18.39	9.59	0.21				FeSO ₄ ·7H ₂ O
19.04	8.70	0.18				FeSO ₄ ·7H ₂ O
19.23	7.52	1.73				FeSO ₄ ·7H ₂ O
20.24	5.73	-0.21	22.96	1.07	0.20	FeSO ₄ ·7H ₂ O
21.30	3.02	-0.53				FeSO ₄ ·7H ₂ O
22.06	2.50	0.31				FeSO ₄ ·7H ₂ O
22.50	1.36	0.63	49.70	0.50	0.45	FeSO ₄ ·7H ₂ O

* Solution obtained by dissolving the alum $K_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 24H_2O$ in water alone.

† Probably, points on a boundary curve of a four-component system.

‡ Probably, points on a boundary curve of a four-component system.

excess of acid and proceed as if dealing with a three-component system, meanwhile acquiring the data necessary to treat the several systems as of four components.

Series were made of aqueous solutions of ferric sulfate and either ammonium sulfate, potassium sulfate, or ferrous sulfate, and agitated continuously in thermostats for upwards of four months. From time to time the liquid phases were analyzed, until they had reached a steady state. The final results for 25°C. are given in table 1. Recalculated to the basis of moles per 100 grams of solution they are plotted on the right-angled isosceles triangle, in figure 1, as offering the best comparisons of them. The data are included for ferric sulfate in aqueous solutions of sulfuric acid, recalculated from analyses by Constable (3).

AMMONIUM SULFATE-FERRIC SULFATE-WATER

The system was studied at 25°C. by J. E. Hunter (5). Much difficulty was encountered in preparing solutions from which basic ferruginous solids would not precipitate on standing. In contact with solutions containing from 1.7 per cent ammonium sulfate and about 44.5 per cent ferric sulfate to 17.3 per cent ammonium sulfate and 16.3 per cent ferric sulfate, the stable solid is the alum $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$. At lower concentrations of ammonium sulfate the solid is a more basic precipitate of iron sulfates, while at higher concentrations the solid is ammonium sulfate. The tie lines for solutions and corresponding residues do not give a perfectly unique crossing for the alum, but ones reasonably close to one another. Analysis of a dry residue gave 41.5 per cent ferric sulfate and 13.6 per cent

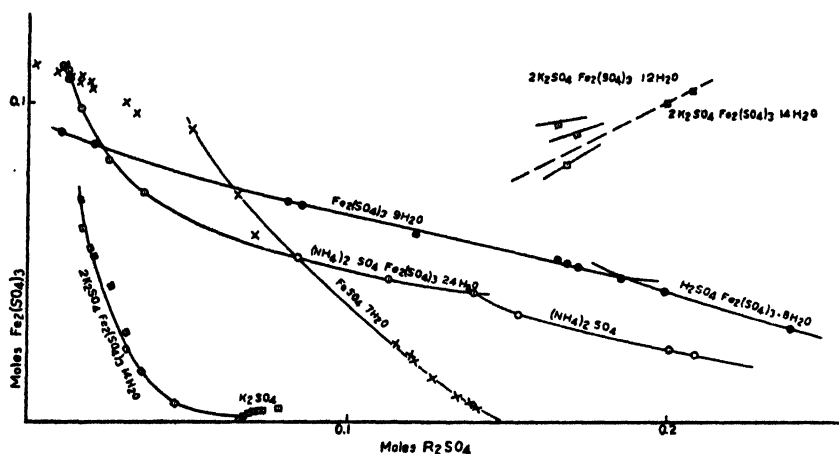


FIG. 1

ammonium sulfate against 41.5 per cent ferric sulfate and 13.9 per cent ammonium sulfate as required by the alum formula.

The ammonium sulfate precipitates were all more or less contaminated by yellow ferruginous solids. A few only in which the contamination was slight are recorded here. To prevent this contamination would require the addition of much sulfuric acid and would markedly affect the solubility of the ammonium sulfate; the system would then become, inevitably, a four-component one. To prove the solid phase was ammonium sulfate, the carefully filtered, clear, mother liquors were placed in contact with solid ammonium sulfate for several days. Analysis of the liquid phase then showing no change in composition, it was concluded they were already saturated with respect to ammonium sulfate when filtered, and the residues were essentially that salt.

It was shown by dilatometer measurements that ammonium ferric alum is stable below 36°C., above which temperature it decomposes.

POTASSIUM SULFATE-FERRIC SULFATE-WATER

This system has been studied by D. A. Pickler (9). According to the International Critical Tables, potassium ferric alum, $\text{K}_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$, is stable to 33°C. (7). In contact with its aqueous solution, Pickler has found that it decomposes above 17°C. to form another double sulfate of potassium and iron with the simultaneous formation of a very basic iron complex of low solubility. Satisfactory crystals of the alum were obtained by crystallizing from solutions at 0°C. and removing adhering mother liquor and basic ferruginous material with filter paper. A series of solutions was prepared, from alum, ferric sulfate, potassium sulfate, and appropriate amounts of sulfuric acid and water, and agitated for four months at 25°C., when a steady state had been realized. The data in table 1 are results of the final analyses. In contact with solutions from 2.83 per cent potassium sulfate and 27.8 per cent ferric sulfate to 11.7 per cent potassium sulfate and 0.8 per cent ferric sulfate the solid phase is a double sulfate. At lower concentration of potassium sulfate the ferric sulfate hydrolyzes with precipitation of a more basic complex, and at higher concentrations the solid phase is potassium sulfate, K_2SO_4 .

A plot of the tie lines between solution and corresponding residue data indicates with reasonable certainty that the double salt contains two reacting weights of potassium sulfate to one of ferric sulfate. On the line through the origin and corresponding to all mixtures in this proportion, points were selected corresponding to different proportions of water of crystallization. Tie lines from the point corresponding to 14 molecules of water of crystallization to the solution points passed more closely to the points for corresponding residues than tie lines from any other point. Consequently, and beyond reasonable doubt, the formula for the double salt is $2\text{K}_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$. The solution and residue designated by an asterisk in table 1 were made from potassium ferric alum and water alone. The plotted tie line passes very close to the point representing the double salt.

The solutions designated by a dagger (†) in table 1 were obtained in an effort to realize a condition where pure potassium sulfate would alone exist in the solid phase. The solubility of this salt evidently increases much more rapidly with addition of sulfuric acid than do the ferric complexes present. A boundary curve, in part, was realized where the solid phases are potassium sulfate and the double salt just described. In the three-component system obtained by keeping excess sulfuric acid at a minimum, the range of concentrations is very short over which potassium sulfate alone is the solid.

FERROUS SULFATE-FERRIC SULFATE-WATER

The literature covering the effects of other sulfates on the solubility of ferrous sulfate has been summarized recently (8). In general, the solubility of ferrous sulfate is depressed in the presence of another sulfate. The formation of double salts is common. At high temperatures only is the hydrolysis of serious moment.

The effects produced by the addition of ferric sulfate to solutions of ferrous sulfate have been studied by C. C. Hudson (5). The data for solutions agitated at 25°C. for seven months are included in table 1. There is a transition point or "constant solution" containing 8.16 per cent ferrous sulfate and 36.6 per cent ferric sulfate. With higher concentrations of the ferrous salt, the stable solid phase in contact with the solutions is $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. With concentrations less than 8.16 per cent ferrous sulfate, the nature of the solid phases is uncertain.

Examination of the data shows, at very low concentrations of ferrous sulfate and hydrogen sulfate in the liquid phase, the solid phase approximates in composition the basic sulfate $\text{Fe}_2\text{O}_3 \cdot 2.5\text{SO}_3 \cdot 7\text{H}_2\text{O}$ recently described or a more basic ferric complex (solid solution) (1). As the concentration of ferrous iron increases in the liquid phase with more hydrogen sulfate the former increases in the solid phase, i.e., ferrous sulfate is a component of the solid phase. One is dealing with a four-component system and two phases are present in a mixture of solids. Calculated as oxides, for treatment as a four-component system, we find the solutions varying from one containing FeO, 0.18 per cent, Fe_2O_3 , 17.9 per cent, SO_3 , 28.26 per cent, and H_2O , 53.64 per cent, to one containing FeO, 2.51 per cent, Fe_2O_3 , 15.37 per cent, SO_3 , 28.94 per cent, and H_2O , 53.18 per cent. The range of concentrations covered is so narrow that graphical treatment is difficult, and the data are insufficient to justify definite statements regarding the composition of the solid ferric complex encountered. In table 2 are the results for a series kept at 50°C. for seven months. Again, at high concentrations of ferrous sulfate the heptahydrate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, is the stable solid. The constant solution at the transition point contains 14.74 per cent ferrous sulfate and 32.94 per cent ferric sulfate. With very low concentration of ferrous sulfate in the liquid, the composition of the solid approaches the basic sulfate $\text{Fe}_2\text{O}_3 \cdot 2.5\text{SO}_3 \cdot 7\text{H}_2\text{O}$, but as the concentration of ferrous iron increases in the liquid it becomes an essential constituent of the solid phase or phases in contact with the liquid. Ferric hydroxide is very slightly soluble in solutions of ferrous sulfate at ordinary temperatures. In table 3 are the results of agitating the hydroxide in contact with solutions of varying composition at 50°C. for seven months. Though small, the solubility is appreciable and increases relatively more as the concentration of the ferrous sulfate increases. The analysis of the residues shows a relatively greater absorption of SO_4 than of ferrous iron

in the solid. Consequently it would seem necessary to assume that basic ferrous sulfates are present in the solids as well as basic ferric compounds. The data for liquids appear to fall on a boundary curve for a four-component system, but the nature of the two coexisting solid phases is indefinite.

TABLE 2

Ferric sulfate in aqueous solutions of ferrous sulfate at 50°C.

LIQUID PHASE			RESIDUE			SOLID PHASE
FeSO ₄	Fe ₂ (SO ₄) ₃	SO ₄ excess	FeSO ₄	Fe ₂ (SO ₄) ₃	SO ₄ excess	
per cent	per cent	per cent	per cent	per cent	per cent	
0.19	48.73	0.78				Basic ferric sulfate
0.67	46.54	2.59	0.49	58.06	-5.82	Basic ferric sulfate
3.67	44.50	1.33				Basic ferric sulfate
6.18	41.03	3.16	11.21	48.33	-6.21	Basic ferric sulfate and FeSO ₄ ·7H ₂ O
6.28	40.53	3.00	11.20	47.69	-6.17	Basic ferric sulfate and FeSO ₄ ·7H ₂ O
8.02	38.87	5.20				Basic ferric sulfate and FeSO ₄ ·7H ₂ O
10.55	36.61	2.50	22.17	46.43	-6.10	Basic ferric sulfate and FeSO ₄ ·7H ₂ O
14.74	32.94	1.09				FeSO ₄ ·7H ₂ O
19.40	25.35	0.95	54.95	10.74	0.30	FeSO ₄ ·7H ₂ O
21.76	19.85	1.01	66.20	4.61	0.20	FeSO ₄ ·7H ₂ O
27.88	9.67	0.22				FeSO ₄ ·7H ₂ O
30.35	5.40	0.30	53.97	2.80	0.51	FeSO ₄ ·7H ₂ O
31.99	2.79	0.67				FeSO ₄ ·7H ₂ O

TABLE 3

Composition of liquids and residues obtained by treating solutions of ferrous sulfate with ferric hydrate

LIQUID PHASE			RESIDUE		
Fe	Fe	SO ₄	Fe	Fe	SO ₄
per cent	per cent	per cent	per cent	per cent	per cent
3.50	0.15	6.34	0.96	40.03	5.95
4.27	0.19	7.61	0.14	38.18	6.80
5.15	0.22	9.55	0.14	38.18	6.80
6.72	0.25	12.00	2.10	45.00	8.43
8.38	0.36	15.47			

In dilute solutions of ferrous sulfate, the system is always a four-component one.

No double salt, nor pseudo alum analogous to that described by Occleshaw, exists between 25°C. and 50°C. at any concentration of ferrous sulfate.

SUMMARY

It is shown that, generally, the addition of ferric sulfate to an aqueous solution lowers the solubility of another sulfate. At extreme dilutions when hydrolysis is nearly complete, sulfates which form disulfates with sulfuric acid, such as ammonium sulfate and potassium sulfate, may become more soluble, but over a very small range of concentration.

With ferrous sulfate, no double salt is formed between 25°C. and 50°C. at any concentration of ferric sulfate.

With ammonium sulfate, an alum is formed below 36°C., and the range of concentrations over which it exists at 25°C. is shown, with approximate accuracy.

With potassium sulfate an alum exists below 16°C. over a wide range of concentration. It is not stable above 16°C., but a double salt, $2K_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 14H_2O$ is stable over all but very high or very low concentrations of ferric sulfate. The concentration limits are shown with approximate accuracy.

At very low concentrations and at rather high concentrations of ferric sulfate in the presence of another sulfate, the system must be treated as composed of four components. But over wide ranges of concentration and temperature the system may be considered as composed of three components, and so treated, practically, with the addition of small excesses of sulfuric acid.

REFERENCES

- (1) BASKERVILLE AND CAMERON: *J. Phys. Chem.* **39**, 769 (1935).
- (2) CAMERON: *J. Phys. Chem.* **34**, 692 (1930).
- (3) CONSTABLE, E. W.: Doctor's dissertation, University of North Carolina, 1934.
- (4) DOBBINS AND BYRD: *J. Phys. Chem.* **35**, 3673 (1931); *J. Am. Chem. Soc.* **53**, 3285 (1931).
- (5) HUDSON, C. C.: Master's thesis, University of North Carolina, 1935.
- (6) HUNTER, J. E.: Master's thesis, University of North Carolina, 1935.
- (7) International Critical Tables: Vol. VII, p. 157. McGraw-Hill Book Co., New York (1926).
- (8) OCCLESIAW: *J. Chem. Soc.* **127**, 2598 (1925).
- (9) PICKLER, D. A.: Master's thesis, University of North Carolina, 1935.

NEW BOOKS

The Next Hundred Years: the Unfinished Business of Science. By C. C. FURNAS. 434 pp. Baltimore: Williams & Wilkins Co., 1936. Price: \$3.00.

Since the death of Slosson how often have we heard the lament that no one has risen to take his place in the popularizing of chemistry. In reading the present book the reviewer became convinced that this complaint need no longer be considered valid, although chemistry constitutes only a small part of the work. A freshness of viewpoint, an originality of treatment, a readiness of wit challenging our most cherished beliefs,—scientific and otherwise,—breadth of outlook and wide scope of subjects, all controlled by sound common sense, have been united with masterly genius.

Although the work makes no claim of especially drawing upon or contributing to the field of physical chemistry, yet frequent use is made of its methods in dealing with the subjects treated, and any physical chemist will profit from and be entertained by this keen analysis of the present status and future problems of science.

The topics are divided between the fields of biology, chemistry, physics, engineering, and sociology. One cannot fail to be impressed by the wide range of knowledge displayed and the variety of problems discussed. The specialist will probably be most interested by the subjects remote from his own field with which he does not so often have contact.

The usefulness and instructive features might have been enhanced by the introduction of some tables, for example, of the vitamins and hormones and their functions.

In spite of the caution and prevailing skepticism of the author, he occasionally displays a surprising degree of confidence in his predictions. Probably few, if any, biologists will show his optimism as to the possibility of unlimited extension of the span of human life, nor many engineers or scientists follow him in believing that the utilization of sunlight as a power source is imminent.

The book is not only thoughtfully written and instructive but is pervaded by an atmosphere of conviction and a sprightliness of presentation that make it a most readable work which can be recommended to any reader who looks to the future with an open mind.

S. C. LIND.

Electrolytic Oxidation and Reduction: Inorganic and Organic. By S. GLASSTONE and A. HICKLING. Vol. IX of a Series of Monographs on Applied Chemistry edited by E. Howard Tripp. 22 x 14 cm.; x + 420 pp. New York: D. Van Nostrand Company, Inc., 1936. Price: \$9.00. London: Chapman and Hall, Ltd., 1935. Price: 25s.

This is a well-balanced monograph on the preparation of inorganic and organic compounds by electrolytic oxidation and reduction, in which the basic theory is presented adequately and a wealth of practical information is to be found. Experimental methods are not discussed in detail, although the various factors affecting yields are treated systematically. Wherever possible the authors try to give an unbiased interpretation of the reaction mechanisms involved. They fully realize the limitations of our present knowledge of the subject. Although many problems

are left unsolved, the discussions given should stimulate further research in this intriguing field.

The first three chapters (ninety-five pages) deal with "Reversible Electrode Potentials," "Polarization and Overvoltage," and "Diffusion Phenomena in Electrolysis." The theory underlying polarization is treated more extensively than in other texts, and is up-to-date. It is not quite clear why the saturated calomel electrode is less advantageous than the 0.1 *N* or 1 *N* calomel electrodes on account of a high temperature coefficient (p. 13). The oxidation potentials of *o*-phenanthroline ferrous iron, and diphenylamine are not known at pH = 7; the data tabulated on p. 31 should refer to acid medium. In the calculation of electrode potentials during electrolysis (p. 72) the migration of ions should have been considered. This is mentioned later, but it would have been more logical to mention this on p. 72.

The following chapters deal with reversible inorganic oxidation and reduction processes, irreversible organic and inorganic reduction processes, "polymerization of anions," oxidation of fatty acids and their salts, irreversible inorganic and organic oxidation processes, and "anodic substitution." An extensive list of literature references is given at the end of each chapter; the patent literature is considered throughout the text. It is regrettable that no attention is paid to the important investigations of Conant and coworkers on the "apparent oxidation potential" of various organic compounds.

The above remarks do not detract from the value of this timely monograph, which is recommended to all those who for theoretical or practical reasons are interested in electrolytic preparations, and in electrode reactions in general.

I. M. KOLTHOFF.

Inorganic Colloid Chemistry. II. The Hydrous Oxides and Hydroxides. By H. B. WEISER. 15.5 x 23.5 cm.; vii + 429 pp. New York: John Wiley and Sons, Inc., 1935. Price: \$4.75.

The second volume in this series by Professor Weiser maintains the same high standard as Volume I. As the subtitle indicates, this work covers about the same field as was covered by the author in his book, *The Hydrous Oxides*, which he published about ten years ago. However the present work is in no sense a revision of the previous one. So much has been accomplished in this field in the ten year period that the work has been almost completely rewritten. X-ray analysis has proved that many of the substances considered to be hydrous oxides at that time are in reality hydrous hydroxides or hydrous oxide hydrates. These results have made extensive changes in the subject matter necessary.

After a general introductory chapter which considers the preparation, properties, and nature of hydrous oxide sols and gels, the author in the next three chapters deals with the hydrous oxides of iron, the aluminum family, and chromium. The hydrous oxides of the other elements are taken up, where practicable, in the order in which they come in the periodic table. The last four chapters deal with technical applications of these important types of substances and are titled "Mordants"; "Color Lakes of the Hydrous Oxides"; "Mineral Tanning"; and "Coagulants in Water Purification." These last chapters add considerably to the value of the book from the technical point of view. Like the first volume of the series, this one is well illustrated and a complete list of references to original work is given.

Those who have used Professor Weiser's previous work on this subject will welcome this new book. It is very complete and up-to-date. Colloid chemists will welcome this second member of the series on Inorganic Colloid Chemistry and will await the appearance of the third volume with interest.

L. H. REYERSON.

Colorimetric Methods of Analysis. Volume I, Inorganic. By FOSTER DEE SNELL and CORNELIA T. SNELL. xxiii + 766 pp. New York: D. Van Nostrand Co., 1936. Price: \$9.50.

Of the physicochemical methods in daily use in analytical laboratories, the colorimetric doubtless hold first place. The size of the present work, compared with that of F. D. Snell's *Colorimetric Analysis*, published in 1921, attests the rapid development of this branch of analysis. The first volume of the second edition embraces a brief account of the principles of colorimetry, a rather full description of colorimetric apparatus, and a comprehensive collection of methods for the colorimetric determination of both the common and the rarer elements; a few turbidimetric and nephelometric methods are included incidentally. A section of some fifty pages is devoted to the determination of hydrogen-ion concentration. Photoelectric colorimeters are described, and their application is discussed; the Pulfrich photometer receives mention.

The book gives evidence of careful preparation, and there are only a trifling number of typographical errors; on page 51, in a footnote, the names of Emich and Donau are incorrectly given. One might wish that the authors had given a fuller discussion of the principles of colorimetry. The volume should prove a useful one for those making use of colorimetric methods. Since the authors have intentionally confined themselves to the practical side of the subject, the book is of little value to those interested in the theoretical aspects of colorimetry.

E. B. SANDELL.

Ueber katalytische Verursachung im biologischen Geschehen. (On Catalytic Causation in Biological Phenomena.) By ALWIN MITTASCH. 14.5 x 22 cm.; x + 126 pp. Berlin: Julius Springer, 1935. Price: 5.70 RM.

This is the publication in an extended form of an article which the author contributed to the periodical *Die Naturwissenschaften* with the subtitle "Auch ein Berzelius-Gedenken," as a tribute to the memory of Berzelius on the occasion of the centenary of the origination by Berzelius of the concept of catalysis in 1835. The present author is a chemist who urges many years experience in technical catalysis as an excuse for entering the field of biological catalysis, while admitting that the last word must rest with biologists. In the course of his review of the problem he deals with a large variety of subjects such as immunity, hormones, growth substances, vitamins, genes, and stimuli of various kinds. The treatment is largely philosophical and in the course of the argument such subjects as holism, causality, vital force, and metaphysics are introduced. A feature of the book is the liberal citation of literature references and of lists of books for further reading. The postscript ends with a quotation from Goethe: "Alles ist einfacher, als man denken kann; zugleich verschränkter, als man begreifen kann" (All things are simpler than one may think; at the same time more interlocked than one can conceive),—a statement which would seem quite appropriately to sum up the author's writing.

P. HAAS.

Les Solutions Concentrées. Théorie et Applications aux Mélanges Binaires de Composés Organiques. By JEAN TIMMERMANS. 647 pp.; 540 figures. Paris: Masson & Cie, 1935.

It is difficult to give the reader an adequate idea of the wealth of material to be found in this book of Timmermans. Not only does he present the theory of various types of binary mixtures of organic substances but he also reproduces, in a very comprehensive manner, experimental data dealing with such properties of the mixtures as density, freezing point, boiling point, critical solution temperature,

refractive index, viscosity, surface tension, etc. The data are sometimes given in tables, but usually by means of accurately drawn graphs.

The book includes a 26-page bibliography and a 49-page formula index of the binary systems discussed in the text.

The usefulness of the book is somewhat impaired by the very individualistic system of symbols used by the author and by the very small type employed for letters and numbers in the graphical figures.

F. H. MACDOUGALL.

Solubility of Non-electrolytes. Second edition. By JOEL H. HILDEBRAND. American Chemical Society Monograph Series. 203 pp. New York City: Reinhold Publishing Corporation, 1935. Price: \$4.50.

The appearance of a second edition of Dr. Hildebrand's well-known book on solubility will be welcomed by those who are familiar with the first edition. They will be glad to have available a portrayal in moderate compass of the progress that has been made during the last dozen years in the study of solutions. Dr. Hildebrand's monograph can be heartily recommended to the attention of all students of the properties of solutions. It is to be noted that only non-electrolytes are treated by the author.

F. H. MACDOUGALL.

Die Fermente und ihre Wirkungen. Supplement Bd I: Spezieller Teil: Hauptteil VII-XV. By CARL OPPENHEIMER. The Hague, Holland: W. Junk Verlag, Scheveningsche Weg 74, 1935-36. Appearing in Lieferung of ca. 160 pp. each, 20.5 x 28 cm. Priced at \$6.80 per Lieferung.

The chemist investigating enzyme reactions is dealing with organic catalysts elaborated by, and controlling the reactions in, living cells and tissues. Naturally the flood of papers appearing in this field is enormous. During 1924-1929 the massive four volumes of the fifth edition of Oppenheimer's *Die Fermente und ihre Wirkung* appeared and have been accepted as the standard reference work in the field of enzyme chemistry.

The present volume deals with the literature which has appeared since the main series of volumes was published. Lieferung 1 to 5 are already published. They maintain the high standards which characterized the parent volumes. No other work of equivalent grade is available in this field. It is encyclopedic in scope and is invaluable to students of enzyme phenomena.

ROSS AIKEN GORTNER.

Fundamentals of Biochemistry in Relation to Human Physiology. Fifth edition. By T. R. PARSONS. xii + 453 pp. Baltimore: William Wood and Company, 1935. Price: \$3.00.

In 1923 the author, a member of the faculty of the University of Cambridge, published the first edition of this *Fundamentals of Biochemistry*. The book represented an "attempt to describe in a continuous story the more important generally-accepted principles which have been derived from the study of the changes occurring in the human body." The author's purpose that "any merit my book may possess may result from its containing less of information rather than more than other books contain" has been successfully achieved and has made this book a welcome novelty in these days when many elementary texts appear to be designed rather to impress fellow scientists with the erudition of the author than to present an "introduction suitable for readers new to the subject."

Despite the large number of important recent advances in biochemistry, the

author has succeeded admirably in maintaining his original objective in this, the fifth, edition. The newer developments in the fields of pigments (flavins), hormones, sterols, and vitamins are presented in a satisfactory manner with excellent citations of the literature for those who would read further.

The reviewer knows of no elementary text in which the relations of physical chemistry to life are presented more simply and more effectively than in the two chapters under the headings of gas tensions, osmotic pressure, colloids, adsorption, the reaction of body fluids, and the functional importance of electrolytes.

While the material presented is neither designed nor adequate in amount for the courses in biochemistry of our professional schools in this country, it affords a worthy introduction to the more comprehensive texts and as such should be readily available for these students. It can also be recommended as an excellent general presentation for the layman who wishes to be informed in modern developments of chemistry as related to vital activity.

HOWARD B. LEWIS.

Flame. By O. C. DE C. ELLIS and W. A. KIRKBY. Methuen's Monographs on Chemical Subjects. 17 x 11 cm.; vi + 106 pp. London: Methuen and Co., Ltd., 1936. Price: 3/ net.

The study of the initiation and propagation of flame in gaseous mixtures has not only become increasingly important in recent years by reason of its relation to the internal combustion engine, but has also received much attention in the research laboratory. The authors deal not only with the physical aspects of combustion but also with such matters as the effect of temperature and pressure on flame equilibria, chain reactions, and free radicals. They give 160 references to literature, including very recent work, and in the space at their disposal they present a review of the subject which is both authoritative and interesting. The illustrations comprise a plate and fourteen diagrams.

J. R. PARTINGTON.

Aluminium-Legierungen. I Teil zugleich Anhang zu Aluminium Teil A in Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. By A. GRUTZNER and G. APEL. 26 x 18 cm.; 342 pp. Berlin: Verlag Chemie, 1936. Price: 26.25 marks (in Germany, 35 marks).

The book gives a list of aluminum alloys classified according to a system, with the compositions, properties, and applications, and references to literature and patents. To the metallurgist and technician it will be of great utility.

J. R. PARTINGTON.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer 4: Stickstoff. Lieferung 3. 26 x 18 cm.; pp. 507-854. Berlin: Verlag Chemie, 1936. Price: 41.25 marks (in Germany, 55 marks).

The present section deals with the oxides of nitrogen. It includes a very detailed discussion of the technical formation of nitric oxide in the electric arc and by the oxidation of ammonia. The latter, as the most important modern process for the manufacture of nitric acid, receives special attention, and this section is perhaps the best and fullest account of the subject which has yet appeared. The rest of the volume is also of high standard and includes many discussions of physicochemical

and technical interest. As an example, the account of the reaction $2\text{NO} + \text{O}_2 = 2\text{NO}_2$, with a wealth of numerical data, may be mentioned.

J. R. PARTINGTON.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer 35: Aluminium. Teil A, Lieferung 3. 26 x 18 cm.; pp. 451-534. Berlin: Verlag Chemie, 1936. Price: 10.50 marks (in Germany, 14 marks).

This section deals solely with the surface treatment of aluminum and aluminum alloys, including oxide layers and metallic surfaces. It gives full references to literature and patents and contains material of physicochemical interest as well as much on the technical side.

J. R. PARTINGTON.

Reactions of Organic Compounds. By W. J. HICKINBOTTOM. 22.5 x 15 cm.; x and 449 pp. London: Longmans, Green and Co., 1936. Price: 16/—.

For its price and size this book is unique. The author has set out to describe the facts of organic chemistry by reference to laboratory practice rather than to classical theory, and in consequence the arrangement of the subject matter presents unusual features. The most obvious is simplicity of classification. Only eleven chapters are taken to describe the reactions of the commoner groupings and radicals in the various types of structural situation in which they occur. The consideration of benzene with methane, phenols and alcohols with enols, etc., in this way avoids repetition and enables the ground to be covered much more neatly than is done in many text-books where the conventional order is followed.

As a typical example the chapter headed "Aldehydes and Ketones" can be mentioned. Here are first detailed quite fully the various transformations of substances of these types without any references to the common subdivisions of organic chemistry, a very widely chosen selection of specific examples is then quoted, drawn from aliphatic, aromatic, and heterocyclic systems, the carbohydrates, and the quinones. Such a plan emphasizes the essential unity of the chemistry of the *carbonyl* compounds, and at the same time the wealth of experimental illustration given affords the very necessary indication of the limitations which "general" reactions are apt to display in practice.

As a complement to a standard text-book this work should prove valuable both to advanced students and to those who desire a book of reference which is convenient to read and up-to-date (the index is good and frequent citations are made to the original literature). From the point of view of the student the book is additionally attractive because it has a useful appendix dealing with the identification of organic substances, and throughout its contents are distributed some thirty five pages of tables of physical constants, derivatives etc., quite adequate for the general requirements of qualitative analysis. Full experimental details are included for several hundreds of preparations. It thus offers under one cover much of the material of three books.

R. J. W. LE FÈVRE.

ERRATUM

VOLUME 40, NUMBER 2

Page 208. In figure 1 the vertical line through G should be extended down to meet the horizontal line joining the batteries. Another cell (total of 4 volts) should be in the grid circuit.

ON THE U-TUBE METHOD OF MEASURING ELECTROPHORESIS

A. L. ROBERTS AND J. C. CARRUTHERS

Department of Physical Chemistry, The University, Liverpool, England

Received January 16, 1936

There is a general impression that electrophoretic data obtained by the U-tube method are not as reliable as those obtained from the observation of individual particles by the aid of the microscope. This impression no doubt has its origin in the fact that in the latter method due allowance is made, by means of the Smoluchowski theoretical treatment, for the influence of the electrosmotic flow of the medium upon the electrophoretic velocity of the suspended particles, whilst in the U-tube case no correction for electrosmosis is applied. Nevertheless the values obtained by the U-tube method are of the anticipated order of magnitude, although it does not appear that any measurements have been carried out hitherto to demonstrate that the electrophoretic velocity directly observed in the U-tube is identical (within the legitimate experimental error) with the velocity obtained by the microscopic cell method. In the present paper a few measurements are recorded which serve to substantiate the belief that the results obtained by the two methods are in fact in satisfactory agreement. This finding, whilst satisfactory in itself, nevertheless raises a problem which cannot at present be accounted for on theoretical grounds. Briefly the point is as follows.

As is well known, in the microscope cell arrangement, which consists essentially of a *closed* cell entirely filled with the suspension, the direction and magnitude of electrophoretic motion of any individual particle depends upon its position at the moment of observation. In general all the suspended particles are sensibly affected by the electrosmotic flow of the medium, which moves in one direction near the walls and in the reverse direction in the central region of the cell. The consequence is that the electrophoretic velocity of a suspended particle near the wall is too small or too great depending upon the sign of the electric charge on the particle, medium, and wall, respectively, whilst at the center a similar erroneous result is obtained but in the opposite sense. There is but one position within such a cell at which the observed electrophoretic velocity is effectively independent of the electrosmotic flow. Ordinarily the suspended particles have the same sign as that on the glass wall of the cell, both being

opposite to that on the liquid medium. In such a case the suspended particles near the wall may actually be carried in a direction opposite to that which would be expected from the sign of their electrophoretically effective charge. All this behavior is apparently well accounted for by Smoluchowski's theoretical treatment.

In the U-tube method no attempt is made to follow the motion of an individual particle. Instead, the rate of ascent or descent of the meniscus is measured, the meniscus being the area of separation of the turbid (or colored) suspension from the transparent medium which occupies the remaining portion (usually the upper portion) of the two limbs of the U-tube. Naturally care is taken to keep the applied potential gradient constant by having the same electrical conductivity maintained throughout the tube proper.

It would be reasonable to expect that in the U-tube arrangement electrosmotic flow of the liquid medium would take place just as it does in the microscope cell. If this is so one would not expect to find, as one does in fact find, a permanent and sharp meniscus or boundary, since the existence of such a boundary implies, or seems to imply, that *all* the particles, independent of their distance from the wall of the tube, are travelling in the same direction with the *same* velocity.

This difficulty was explained, or rather explained away, by the suggestion that in a U-tube of ordinary dimensions the electrosmotic effect though present had not time to bring about any observable disturbance during the time usually taken for a set of moving boundary readings (about thirty minutes). This, however, seems to be ruled out by the observations of Gilford (2), who used a tube of ordinary dimensions and observed microscopically the movements of individual particles,—the tube being *entirely* filled with the suspension, however. The same behavior was observed as in the microscopic cell, i.e., the direction and magnitude of the velocity of individual particles was a function of their distance from the wall, this effect being naturally attributed to electrosmotic streaming of the medium, and furthermore such disturbances set in as soon as the external field was applied. Again, from an expression given by Lamb (3) it can be calculated that surface disturbances would reach the center of a tube of radius of the order 0.5 cm. in approximately six seconds. The difficulty of accounting for the existence of a sharp boundary between suspension and supernatant liquid remains.

In the ordinary U-tube arrangement the surface of liquid in each limb is free, and consequently electrosmotic movement of the medium would be expected to produce a head in one of the limbs. This effect, though not ordinarily observable, has in fact been observed by the use of a U-tube with constricted end (4). In the microscope method, as well as in Gilford's arrangement of a single vertical tube, there is no "free" surface.

The experiment has therefore been tried by the present writers in which a closed U-tube completely filled with liquid was employed. Again precisely the same result was obtained as with the ordinary open U-tube arrangement. Further, as it was just conceivable that the apparent automatic elimination of the electrosmotic flow might be connected with the fact that the suspension occupied the bent portion of the U-tube, measurements were carried out in which the suspension occupied a position in the vertical limbs with medium both above and below. Here four boundaries can be observed. Once more the same results were obtained as before.

We are not in a position to offer any explanation of the apparent elimination of the electrosmotic effect in the U-tube measurements as ordinarily carried out. Nevertheless, our measurements, which are briefly recorded in tables 1 and 2, justify us in regarding the observed velocities obtained by this method as reliable, in that they agree with the results obtained by the microscopic cell method.

ELECTROSMOSIS MEASUREMENTS

Electrosmotic velocity of water and citrate solutions against quartz and various types of glass

The apparatus was of the moving bubble type. The main electrodes, which consisted of two 3.5 *N* calomel electrodes, were connected by bridges (3.5 *N* potassium chloride in 5 per cent agar-agar gel) with the U-tube (1.5 cm. diameter) which contained the plug. On either side of the plug was a platinized platinum auxiliary electrode used to determine, and to keep constant, the p.d. across the plug. The indicator capillary connected the two limbs of the U-tube, the whole apparatus being completely filled with solution. The quartz of the plug was crushed in an iron mortar and, after obtaining particles which passed an 88-mesh sieve but were retained by a 100-mesh sieve, was thoroughly cleaned.

The mobility under unit potential gradient is given by:

$$v = \frac{V}{H} \cdot k$$

where V = volume of liquid transported in unit time, H = p.d. across plug, and k = "cell constant" of plug, i.e., the ratio of the effective length to the effective cross section.

The value of k was determined by filling the U-tube with *N*/10 potassium chloride and determining the conductivity across the plug by the bridge method. The conductivity measurements were reproducible to within 5 per cent on reforming the plug. The electrodes used in the determinations of k were the auxiliary electrodes of the electrosmosis experiments.

It will be seen that the magnitude of these mobilities is of the same order as the electrophoretic mobilities measured.

ELECTROPHORESIS MEASUREMENTS

Initial curvature of the boundary

A glass U-tube of the Burton type, having a bore of 0.6 cm., was set up and into this was introduced water, as supernatant liquid, and a 0.4 per cent tristearin emulsion. The latter was electrolyte-free in order that the electrosmotic effects should be great. The electrodes were a lead anode and a lead monoxide cathode, to prevent gas formation.

TABLE 1

Electrosmotic mobility of sodium citrate solutions against quartz

CONCENTRATION OF SODIUM CITRATE	P.D. ACROSS PLUG	CURRENT	TIME FOR BUBBLE TO TRAVERSE 14.7 CM.	MOBILITY
<i>millimoles per liter</i>	<i>volts</i>	<i>milliamperes</i>	<i>seconds</i>	<i>cm./sec./volt/cm</i>
0	204	0 1	102	71.0×10^{-5}
1	142.5	1 1	232	44.4×10^{-5}
2	142.5	2 1	277	38.5×10^{-5}
4	142.5	4 5	306	35.5×10^{-5}
10	112	6 4	202*	23.7×10^{-5}

* Over a distance of 5 cm.

TABLE 2

Electrosmotic mobility of water against various types of glass

GLASS	MOBILITY
	<i>cm./sec./volt/cm</i>
Soda glass.....	66.8×10^{-5}
Jena glass.....	70.0×10^{-5}
Pyrex.....	59.5×10^{-5}

A P.D. of 60 volts was applied, the boundaries being observed through a telescope. After two minutes, a distinct curvature of the boundaries was observable, the rising boundary becoming convex and the falling one concave. Thereafter each meniscus retained its shape. It is not improbable that this initial change in the boundary is an electrosmotic effect, especially in the light of the result obtained from Lamb's equation.

Electrophoresis of gelatin

Abramson (1) has measured, by the microscopic method, the electrophoretic mobility of silica particles covered with gelatin in acetate buffers. The following determination of the mobility, in acetate buffers, of kieselguhr particles covered by gelatin was made, using the U-tube method.

This U-tube was fitted with side-arms carrying the current-bearing electrodes. The anode was of zinc and the cathode of lead coated with lead peroxide, thus eliminating gas formation and the accompanying disturbances. Small platinum electrodes in the main U-tube were used to determine the potential gradient.

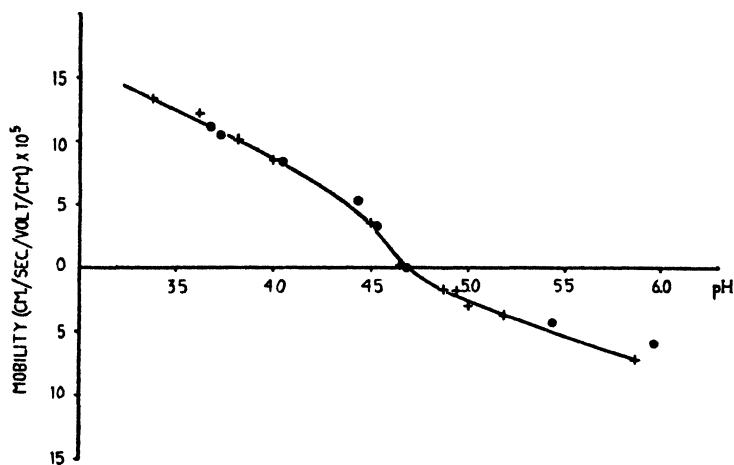


FIG. 1. Electrophoretic mobility of gelatin in *N*/150 acetate
+, Abramson; O, Roberts and Carruthers

TABLE 3
Electrophoretic mobility of gelatin in N/150 sodium acetate

pH	MOBILITY
	<i>cm./sec /volt/cm</i>
5.96	6.1×10^{-5} towards anode
5.43	4.5×10^{-5} towards anode
4.68	No movement
4.53	3.14×10^{-5} towards cathode
4.43	5.2×10^{-5} towards cathode
4.05	8.4×10^{-5} towards cathode
3.73	10.5×10^{-5} towards cathode
3.68	11.1×10^{-5} towards cathode

The gelatin used was Digestive Ferments Co.'s "Bacto-Gelatin." The concentration of the sol was similar to that used by Abramson (0.4 per cent). To this sol was added 4 g. of finely divided, purified kieselguhr, and the whole well stirred and allowed to stand overnight.

In the preliminary work an attempt was made to use, as supernatant liquid, a buffer of the same ionic concentration as the buffered suspension, but containing no gelatin. However, the buffering properties of the gela-

tin were sufficiently great to alter the pH appreciably, and to avoid any error due to this or to the fact that the rising boundary would be moving in a medium of different viscosity to that of the falling boundary, it was found convenient to employ as supernatant liquid a gelatin sol, identical in concentration and buffered in the same manner as the kieselguhr suspension.

The buffer employed was $N/150$ sodium acetate. Over the pH range examined the ionic strength of the sol was maintained constant. This was effected by making the sol $N/150$ with respect to sodium acetate and adding increasing amounts of acetic acid. To each 100 cc. of dispersion 2 g. of sucrose was added to increase the specific gravity. It was observed that after adding the electrolyte to the dispersion there was a noticeable rate of settling in the U-tube. As the mean of an upward and a downward movement was taken in each case, the error due to this must be very small.

pH determinations were carried out in every case by means of the hydrogen electrode.

The results obtained are given in table 3 and plotted with those of Abramson in figure 1.

It must be concluded from the very fair agreement obtained, that in the U-tube apparatus corrections for electrosmosis are unnecessary and that the values of the mobilities obtained by this method are very close to the absolute values.

SUMMARY

It is shown that measurements carried out by the U-tube method, without any correction for the electrosmotic flow of the medium, agree satisfactorily with those obtained by the microscopic cell method where such correction is necessarily introduced.

No attempt is made at present, however, to solve the theoretical difficulty inherent in this finding.

REFERENCES

- (1) ABRAMSON: J. Gen. Physiol. **15**, 575 (1931).
- (2) GILFORD: Phil. Mag. **19**, 853 (1935).
- (3) LAMB: Hydrodynamics, 6th edition, p. 592, equation 20.
- (4) MONAGHAN AND WHITE: J. Phys. Chem. **39**, 935 (1935).

THE VISCOSITY OF SODIUM AMALGAMS

HENRY E. BENT AND NORMAN B. KEEVIL

Mallinckrodt Chemical Laboratory, Harvard University, Cambridge, Massachusetts

Received January 31, 1936

Paranjpe and Joshi have suggested that the properties of liquid sodium amalgams may be most readily accounted for by assuming that the solution is colloidal. They (8) enumerate a large number of phenomena which may be easily explained on the colloidal hypothesis. The case for the idea that dilute amalgams are true solutions has been stated by one of us (1) and further comments in favor of the colloidal point of view presented by Joshi (3).

Two questions arise from this discussion which can be treated to some extent independently. The first is the question of the number of variables required to define a sodium amalgam. If Paranjpe and Joshi are correct in their assumption that temperature, pressure, and concentration are not sufficient to define completely the properties of an amalgam but that the method of preparation and the previous history are also important, then practically all physical measurements on sodium amalgams are of little value, as attention has usually not been directed to these last conditions. In order to evaluate the enormous amount of data on sodium amalgams this question must be answered, and it is a question which can be answered by relatively simple experiments.

The second question has to do with the structure of a liquid sodium amalgam. If the answer to the first question should turn out to be that properties depend not only on temperature, pressure, and composition but also on the physical history of the amalgam, then the presumption would be that the structure is colloidal. If, on the other hand, the answer should turn out to be that the properties of amalgams are completely determined by the temperature, pressure, and composition, then the strongest evidence for the colloidal point of view will have been removed.

Paranjpe and Joshi report results of two types of experiments which indicate that the properties of amalgams change with time. They describe briefly the results of Barave on the change of viscosity with time. This work was later reported in a note (7). Barave finds that the viscosity decreases from 10 to 20 per cent if amalgams are kept for two or three days without agitation. It is also reported that a scum or "cream" forms on the amalgam which disappears on shaking, only to re-form on standing.

The viscosity is restored to its original high value by shaking. These results are sufficiently striking to warrant serious consideration of the colloidal hypothesis. Since previous workers in this field have reported no scum formation when the apparatus was free from oxygen and water (1, 5, 6), it seemed worth while to attempt to repeat the experiments of Barave under a variety of conditions in order to determine whether or not the change in viscosity with time and the formation of a scum is a general property of sodium amalgams.

EXPERIMENTAL

In order to avoid contamination of the amalgam all experiments were carried out in glass apparatus free from stopcocks or rubber connections. The glass was heated and evacuated with a mercury diffusion pump at the beginning of each experiment, until the pressure was about 10^{-5} mm. as measured by a McLeod gauge. Amalgams were prepared by the method used by Paranjpe and Joshi, namely, the electrolytic procedure described by Richards (9) and by the distillation method of Lewis and Kraus (6). The mercury was purified by repeated washing with nitric acid in an apparatus of the type described by Hildebrand (2), and the sodium carbonate used in the electrolysis was recrystallized. The amalgam prepared by electrolysis was introduced directly into the viscometer and the latter then sealed off, eliminating stopcocks.

The data reported by Paranjpe and Joshi give no idea of the dimensions of the capillary or the time of flow. We, therefore, constructed a number of viscometers of such dimensions as to have always a velocity of flow well below that which would give turbulence. Since Barave's experiments indicate that the viscosity is restored to its original value by shaking, it seemed possible that flow through the capillary would have the same effect to some extent and therefore that a small head of amalgam would be desirable if one were to repeat his experiments. Several viscometers were, therefore, constructed with the two bulbs of the viscometer as close together as possible while still having one bulb directly over the other. A capillary 12–19 cm. long with a bore ranging from 0.03–0.05 mm. extended well below the lower bulb and was connected to it by a vertical tube of 6-mm. diameter. This type of viscometer, however, was not free from an objection. At the end of a determination the apparatus was inverted and the amalgam allowed to flow back into the original bulb where it remained without agitation until the beginning of another run. At the beginning of a run the instrument had to be turned into a vertical position. This agitation might be equivalent to the vigorous shaking after which Barave found the viscosity returned to the high value. We therefore constructed the apparatus shown in figure 1 which permitted the amalgam to be held for any desired length of time in the upper bulb and then, without

agitation of the amalgam which was to flow through the capillary, the viscometer could be started by simply raising the glass plunger from the lower part of the viscometer. This avoided any possible objection on the ground that the amalgam was unnecessarily agitated before beginning a determination. The plunger was raised by means of a glass float in the

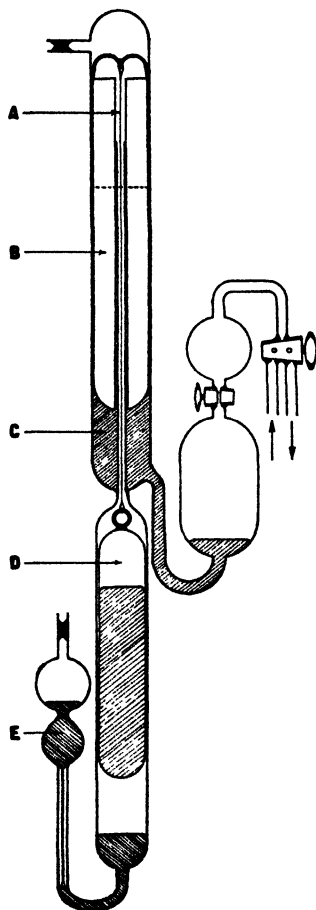


FIG. 1. Vacuum viscometer. A, nickel wire; B, float; C, mercury; D, plunger; E, amalgam, 10 cc. Vertical dimensions have been multiplied by $1/8$ and horizontal dimensions by $1/4$.

upper part of the apparatus, which was in turn raised by admitting mercury to the upper chamber, a nickel wire connecting this float with the glass plunger. At the conclusion of a run the mercury was removed from the upper chamber by evacuation of the bulb and the amalgam returned to the upper bulb of the viscometer. All measurements were carried out in a glass thermostat at $25 \pm 0.01^\circ\text{C}$.

EXPERIMENTAL RESULTS

Our results may be summarized very briefly. We have found no indication of any variation of the viscosity of sodium amalgams with time, and not the slightest trace of scum formation on standing. When working with the most concentrated amalgams we did observe large crystals floating on the surface of the amalgam, but these had no effect on the viscosity unless small crystals were present in such large amounts as clearly to plug the capillary. The amalgam would then drain away from them and leave a mass of crystals in the capillary. We expected to find the best evidence

TABLE 1
Viscosities of dilute sodium amalgams

METHOD OF PREPARATION	MOLE FRACTION OF SODIUM	TIME SINCE PREPARATION	TIME AT REST BETWEEN RUNS	TIME OF FLOW	VISCOSITY RELATIVE TO MERCURY
		<i>hours</i>	<i>hours</i>	<i>seconds</i>	
Electrolytic	0.0289	2.5	1.25	254	1.134
		3	<0.2	253	
		12.5	9.5	254	
		12.75	<0.1	254	
		37	23.5	254	
		37.25	<0.2	253.5	
Distillation	0.0513	1.5	1	296	1.439
		2	<0.2	294.5	
		97.5	95.5	295.5	
		169.5	72	295.5	
		171	<0.2	295	
Mercury added to the above amalgam, shaken and stirred		173.5	1	296.5	
		176.5	3	296.2	
		294	117	296.5	
Same amalgam, shaken and stirred		294.5	<0.1	296.2	
		390	95.5	296.5	
		1449	1059	300	(See text)

of a change in viscosity with time when the amalgams were nearly saturated, but the data recorded in table 1 give no evidence of such an effect.

In addition to the data reported in table 1, similar results were obtained on seven amalgams using the simple type of apparatus first described above. The time between runs varied from twenty minutes to sixty-five days.

The last datum recorded in table 1 was obtained by adjusting the amalgam level so that the upper surface was at the point in the capillary at which the initial time was usually taken. The plunger was then raised

as rapidly as possible and the time determined as usual. Obviously a little time was lost in raising the plunger and in establishing a constant rate of flow of the amalgam. The purpose of this experiment was to reduce all stirring to an absolute minimum before starting a measurement. As will be observed, there is no indication of a decrease in viscosity.

We have observed some of these viscometers for more than two years and can report that the surface is as clear and clean to-day as the day they were prepared and as clean as any surface of pure mercury as far as one can detect by observation.

DISCUSSION OF RESULTS

Our experimental results are in complete disagreement with those reported by Paranjpe and Joshi. From our experiments one would conclude that the properties of sodium amalgam are uniquely determined by the temperature, pressure, and concentration. In favor of Barave's experiments, however, it must be pointed out that he observed certain reproducible phenomena which we have not found, and hence our results may be disposed of by saying that negative results do not disprove one good set of positive experiments. It must be emphasized, however, that the variation in viscosity observed by Barave was very large, and that with many kinds of apparatus and different methods of preparing amalgams we were unable to find this effect. Our results indicate that it would not be profitable for us to search further to reproduce the results of Barave. It is to be hoped that the experiments of Barave will be repeated and, if his results be confirmed, that sufficiently explicit directions be given to permit repetition of the experiments in other laboratories.

With regard to the question of whether sodium amalgam is colloidal or not, it would seem rather unprofitable to consider this question further until the experimental facts are clearly established. We have corresponded with Joshi regarding this problem, and I think we agreed that the viscosity behavior and scum formation were among the strongest arguments in favor of the colloid hypothesis.

It has been reported by Köhler (4) that silver and copper amalgams form amalgams which change in viscosity with the time. These experiments, however, have no bearing on the properties of liquid amalgams, as the amalgams used by Köhler contained much more than enough copper or silver to produce a saturated amalgam. The solubility of copper is given by Richards (10) as 0.0024 per cent at 15°C. and the solubility of silver is given by Tamman and Stassfurth (11) as 0.08 per cent at 20°C. The amalgams investigated by Köhler ranged in concentration from 0.3 to 1.0 per cent and therefore must have contained a great deal of the solid phase.

In order to find if possible a variation in the viscosity of liquid silver amalgams with time we prepared four amalgams by a variety of methods.

In no case did we obtain a variation on standing of as much as 0.25 per cent, which was our experimental accuracy in measuring the time. Only when the amalgams had not been carefully filtered did we observe a decrease of the viscosity with time.

CONCLUSIONS

1. The viscosity of liquid sodium and silver amalgams is found to be independent of time.
2. No scum forms on sodium amalgams when kept in glass containers which have been properly baked and evacuated.
3. These experiments lessen the probability that sodium amalgams are colloidal.

REFERENCES

- (1) BENT: J. Phys. Chem. **37**, 431 (1933).
- (2) HILDEBRAND: J. Am. Chem. Soc. **31**, 933 (1909).
- (3) JOSHI: Indian J. Physics **9**, 153 (1935).
- (4) KÖHLER: Kolloid-Z. **64**, 200 (1933).
- (5) LEWIS, ADAMS, AND LANMAN: J. Am. Chem. Soc. **37**, 2656 (1915).
- (6) LEWIS AND KRAUS: J. Am. Chem. Soc. **32**, 1459 (1910).
- (7) PARANJPE: Indian J. Physics **7**, 95 (1933).
- (8) PARANJPE AND JOSHI: J. Phys. Chem. **36**, 2474 (1932).
- (9) RICHARDS AND CONANT: J. Am. Chem. Soc. **44**, 601 (1922).
- (10) RICHARDS, WILSON, AND GARROD-THOMAS: Carnegie Inst. Wash. Pub. **118**, 172 (1909).
- (11) TAMMAN AND STASSFURTH: Z. anorg. Chem. **143**, 357 (1924).

THE DETERMINATION OF SURFACE CONDUCTANCE FROM MEASUREMENTS ON SUSPENSIONS OF SPHERICAL PARTICLES

HUGO FRICKE AND HOWARD J. CURTIS

The Walter B. James Laboratory for Biophysics, The Biological Laboratory, Cold Spring Harbor, Long Island, N. Y.

Received February 13, 1936

As the particle size of a suspension of an insulating material is decreased, the surface conductance at the particle-water interphases plays an increasingly important rôle in determining the electric conductance of the suspension, and with particles a fraction of a micron in diameter, suspensions can readily be prepared in which the suspended particles add more to the conductance than the same volume of the suspending fluid. We have, for example, prepared suspensions of kaolin with a particle size of about 0.25 micron in diameter, whose conductance was more than twice that of the fluid obtained after removal of the suspended material by centrifugation.

The use of suspensions presents many advantages in the measurement of surface conductance. It is important for the theoretical discussion that we can determine the electrokinetic potential at the interphase directly on the suspension used for the conductance measurements by a determination of the cataphoretic velocity of the suspended particles. So far, suspensions of particles down to 0.25 micron in diameter have been studied. Measurements on still finer suspensions would be interesting, since here the thickness of the diffuse double layer should become apparent in the results. We need, however, a more powerful centrifuge to be able to separate these particles from the suspending fluid. In the following, a preliminary study of the method is presented.

Largely because the subject of surface conductance had its origin in Smoluchowski's (9) theoretical treatment of the diffuse double layer, it has been tacitly assumed in experimental studies of the subject that the aqueous interphase can with sufficient accuracy be represented as a pure conductance. Actually, this is not always the case. Each element of interphase is also the seat of a reactance (4), so the interphase should be represented by a complex admittance¹ which, per square centimeter of interphase, may be expressed as $\sigma_s + jC_s\omega$, where σ_s may be termed the

¹ The admittance is the reciprocal of the impedance.

surface conductivity and C_s , the surface capacity. $\omega = 2\pi n$, where n is the frequency. Since $C_s\omega$ is not necessarily negligible compared to σ_s , an error may be introduced by deriving σ_s from pure conductance measurements, but these should be replaced by measurements of complex admittance; that is, both the conductance and the dielectric constant of the systems under investigation should be determined. This has been the method used, although since the influence of C_s has been negligible in our measurements only the conductances need be considered. A general study of complex surface admittance will be presented elsewhere. The remark may be added that since C_s varies with the frequency, σ_s will contain (3) a term dependent upon the same mechanism which produces C_s , and therefore in such cases where the influence of C_s is appreciable not only is it impossible to measure σ_s without considering C_s , but also the theoretical discussion of the former must involve the latter.

Most of the present measurements were made on suspensions of glass spherules prepared from powdered Pyrex glass which was blown through a blow torch (2). The material was obtained through the courtesy of Dr. L. D. Bishop of the Bureau of Standards. The glass was washed, over an extended period, in distilled water and thereafter equilibrated with the solutions to be used. Two series of experiments have been made, one with solutions of potassium chloride of strength varying from 0.0001 to 0.01 mole per 1000 cc., another less complete with solutions of hydrochloric acid.

The conductance and dielectric constant were measured at frequencies between 1/2 and 100 k.c. with a bridge, using a substitution method. The electrolytic cell containing the suspension is compared with a cell filled with a solution of potassium chloride, the difference in dielectric constant being compensated for by a parallel condenser, while equality of resistance can be obtained by varying the distance between the electrodes in the comparison cell. The resistance of the potassium chloride is measured by comparison with a low inductance resistance box, this measurement being made at low frequency. The influence of electrode polarization, though negligible in the present measurements, could be eliminated by measuring at different electrode distances.

The electrolytic cell containing the suspension has the form of a test tube, with the electrodes sealed into its upper portion. After the measurement on the suspension has been made, the cell is placed in the centrifuge and the suspended matter separated. The liquid between the electrodes now is the suspending fluid, and thus without removing the suspension from the conductivity cell the conductance of the suspending fluid can be measured. This procedure is convenient when working with dilute solutions for which contact with the carbon dioxide of the air must be prevented. The measurements were made at a temperature of 21.4°C.

The value of the surface conductance is calculated by making use of a formula derived by Maxwell (6). This formula gives the conductance (K) of a suspension of spherical particles each of which is composed of a sphere (radius a and specific conductance K_2) surrounded by a concentric spherical shell (thickness t and specific conductance K_3). The formula reads:

$$\frac{\frac{K}{\bar{K}_1} - 1}{\frac{K}{\bar{K}_1} + 2} = \rho \frac{\frac{\bar{K}_2}{\bar{K}_1} - 1}{\frac{\bar{K}_2}{\bar{K}_1} + 2} \quad (1)$$

with

$$\bar{K}_2 = K_3 \frac{(2K_3 + K_2)(a + t)^3 - 2(K_3 - K_2)a^3}{(2K_3 + K_2)(a + t)^3 + (K_3 - K_2)a^3} \quad (2)$$

and where K_1 is the specific conductance of the suspending fluid and ρ is the volume concentration of the suspension.² For the present case, we use $K_2 = 0$ and, assuming the thickness t of the region from which the surface conductance is derived as small compared to the diameter of the suspended particles, we can take

$$(a + t)^3 = a^3 + 3ta^2$$

and consequently

$$\bar{K}_2 = \frac{2tK_3}{a} \quad (3)$$

Defining the surface conductivity σ_s by $\sigma_s = tK_3$ we obtain from equations 1 and 3

$$\sigma_s = \frac{\left(\frac{K}{\bar{K}_1} - 1\right) + \frac{\rho}{2} \left(\frac{K}{\bar{K}_1} + 2\right)}{\rho \left(\frac{K}{\bar{K}_1} + 2\right) - \left(\frac{K}{\bar{K}_1} - 1\right)} K_1 \cdot a \quad (4)$$

For the determination of the volume concentration ρ , two methods have been used. One depends on measurements of the specific density of the suspension (δ) and of the suspending fluid (δ_0), the value of the volume concentration being calculated from

$$\rho\delta_1 + (1 - \rho)\delta_0 = \delta$$

where δ_1 is the specific density of the glass spherules, measured with a pycnometer.

² The same formula is used for calculating the complex surface admittance, replacing conductances in the formula by the corresponding complex admittances.

The second method for determining ρ is indirect but more convenient. It consists in adding solid potassium chloride to the suspension, enough so that the influence of the surface conductance on the conductance of the suspension is inappreciable, and thereafter the conductances of the suspension (K) and suspending fluid (K_1) are measured and the volume concentration ρ_1 of this suspension calculated by Maxwell's formula (equation 1 with $\bar{K}_2 = 0$):

$$\frac{1 - \frac{K}{K_1}}{\frac{K}{K_1} + 2} = \frac{\rho_1}{2}$$

The volume concentration ρ of the original suspension is thereafter obtained by introducing a slight correction for the volume change due to the addition of the salt.

In table 1 is shown a comparison of the two methods.

The diameter of the spherules was determined by counting the number of spherules present in a known volume of a suspension of known volume concentration. The counting was carried out with a ruled chamber such as is used for counting blood cells or bacteria. The value obtained for the diameter was $2a = 1.7\mu$.

The results are given in table 2. The surface conductances are practically independent of the frequency between 1/2 and 100 k.c.,³ showing, however, a slight decrease as the frequency is decreased (4). In the case of the dilute solutions, when the suspended glass is added to the solution of the electrolyte with which it is being equilibrated, one observes a rise in conductance, rapid at first and gradually slowing down. This happens even after prolonged washing of the glass with the electrolyte and is probably due to the solution of the glass. For this reason, when the measurements were made there was an appreciable quantity of foreign electrolytes (besides the hydrogen and hydroxide ions) present, amounting in the most dilute solutions to about 10 per cent in equivalent conductance. The concentrations of potassium chloride and hydrochloric acid given in the second column of table 2 are those required to account for the actually observed conductances of the suspending fluid.

The following measurements were made to determine whether the values obtained for the surface conductance show any dependence on the size of the suspended particles. These measurements were made on kaolin spherules, obtained through the courtesy of Dr. F. S. Brackett of Research Associates Incorporated. Two different particle sizes were used, with diameters of $2a = 0.6\mu$ and $2a = 3.4\mu$, respectively, and the suspen-

³ At higher frequencies σ_s shows a marked increase (5).

sions were made up in a solution of sodium carbonate. The results are shown in table 3. A somewhat smaller value for σ_s is obtained for the

TABLE 1

Comparison of percentage volume concentrations, determined by (1) specific density and (2) electrical conductance

SUSPENDED MATERIAL	VOLUME CONCENTRATION IN PER CENT FROM	
	Specific density	Conductivity
Pyrex spheres.	34 2	34 2
Pyrex spheres. ...	28 4	28 7 28 0
Kaolin spheres. .	10 2 9 9	10 2 10 2

TABLE 2

Measurements on suspensions of glass spherules (diameter $2a = 1.7\mu$) in solutions of potassium chloride and hydrochloric acid

SUSPENDING FLUID	CONCENTRATION IN MICROMOLES PER 1000 CC	VOLUME CONCENTRATION PER CENT ρ	CONDUCTIVITY ($\text{OHMS}^{-1} \text{CM}^{-1}$)		ELECTROPHORETIC POTENTIAL (IN MV) ξ	SURFACE CONDUCTIVITY (OHMS^{-1})	
			Suspension K	Suspending fluid K_1		Observed	Calculated
KCl	169	33 0	18.42×10^{-6}	23.14×10^{-6}	-74	0.45×10^{-9}	0.21×10^{-9}
KCl	470	21.9	50.35×10^{-6}	64.10×10^{-6}	-74	0.58×10^{-9}	0.35×10^{-9}
KCl	930	27 7	86.7×10^{-6}	126.8×10^{-6}	-78	0.58×10^{-9}	0.54×10^{-9}
KCl	1900	26 5	172.2×10^{-6}	251.6×10^{-6}	-73	0.86×10^{-9}	0.68×10^{-9}
KCl	7900	28.4	$675. \times 10^{-6}$	1042×10^{-6}	-70	1.8×10^{-9}	1.25×10^{-9}
HCl	90	25 8	27.80×10^{-6}	35.95×10^{-6}	-42	0.42×10^{-9}	0.21×10^{-9}

TABLE 3

Measurements on suspensions of kaolin spherules in sodium carbonate

DIAMETER OF SPHERULE (10^{-4}CM)	VOLUME CONCENTRATION PER CENT ρ	CONDUCTIVITY ($\text{OHMS}^{-1} \text{CM}^{-1}$)		SURFACE CONDUCTIVITY (OHMS^{-1}) σ_s (obed.)
		Suspension K	Suspending fluid K_1	
0 6	12.65	46.3×10^{-6}	51.0×10^{-6}	0.30×10^{-9}
3 4	37.0	29.7×10^{-6}	51.0×10^{-6}	0.40×10^{-9}

smaller sized spherules, but the difference is not outside the present limit of experimental error.

For the experiments with glass spherules, the measured surface conductances were compared with the theoretical values derived on the assumption that the surface conductance represents the conductance of the ions of the diffuse double layer. Including the electrosmotic term, the surface conductance for an electrolyte completely dissociated into two monovalent ions, is given (1, 8) by:

$$\sigma_s = \frac{D^{3/2}(KT)^{3/2}\sqrt{n}}{2\sqrt{2}\pi^{3/2}\eta\epsilon} \left[e^{-\frac{\epsilon\zeta}{2KT}} + e^{\frac{\epsilon\zeta}{2KT}} - 2 \right] + \sqrt{\frac{DKTn}{2\pi}} \left[u_1 e^{-\frac{\epsilon\zeta}{2KT}} + u_2 e^{\frac{\epsilon\zeta}{2KT}} - (u_1 + u_2) \right]$$

where K is Boltzmann's constant, T the absolute temperature, ϵ the electronic charge, ζ the electrokinetic potential, and n the number of cations or anions per cubic centimeter. For D , the dielectric constant, and for η , the coefficient of viscosity, of the diffuse double layer, we have used the values for water ($D = 79.9$; $\eta = 0.0098$). The quantities u_1 and u_2 are the ionic mobilities of the cations and anions respectively. For these values we have used those obtained at infinite dilution.

The electrokinetic potential, ζ , has been determined by measuring the electrophoretic velocity of the suspended particles by the moving boundary method. In carrying out this determination the suspension used for the conductance measurement was diluted with the suspending fluid, a suspension of about 1 per cent volume concentration being most suitable. The dilution did not appear to change the electrophoretic velocity, as far as could be learned by changing the degree of dilution from several per cent to a fraction of 1 per cent. The suspending fluid also formed the electrical connection between the suspension and the electrodes of the cataphoresis cell. The gravimetric movement of the boundary amounted to from 5 to 10 per cent of the electrophoretic velocities and was compensated for by taking readings with the boundary moving in both directions and averaging. Since the conductance of the suspension and suspending fluid differ by only 1 or 2 per cent, the electric field can be taken as uniform between the electrodes. The value of ζ is calculated from

$$v = \frac{\zeta D}{4\pi\eta}$$

where v is the electrophoretic velocity per unit field strength.

The theoretical values of σ_s given in table 2 are calculated on the basis of the concentrations of electrolytes given in the first and second columns. As remarked above, for the dilute solutions, these concentrations represent only approximately the composition of the suspending fluid, being actually the equivalent values derived from the observed conductances. For the

present, however, this method of calculation is of sufficient accuracy. It should be pointed out that in the case of the potassium chloride solutions the influence of the hydrogen ion is negligible, since these solutions are slightly alkaline. The observed values of σ_s are of the order of 50 per cent higher than the theoretical ones, a deviation in the same direction, although smaller, as found in other recent experimental studies of this subject (7, 10).

The present measurements should be considered as preliminary, and there will be some question as to how great the errors are until a more complete study has been made. It should also be recognized that the present theory for the conductance of the diffuse double layer contains a certain amount of simplification and approximation. This leaves considerable uncertainty as to the exact extent to which the observed surface conductance exceeds that contributed by the diffuse double layer, although the reality of an excess must be allowed. As has already been noted, there is a slight decrease of the surface conductance with decreasing frequency and the excess conductance would therefore be smaller (and might disappear) at zero frequency. The most likely explanation of an excess conductance would be that it is due to the participation of the solid surface in the transport of the current. The presence of the surface capacity (4) itself shows that there is a transport of current at the interphase besides that considered in the present theory of the diffuse double layer. The fact that the surface capacity varies with the frequency requires this surface capacity to be associated with a conductance, the value of which can in certain cases be calculated theoretically when the surface capacity is known as a function of the frequency (3). We find that the observed change of the surface conductance with frequency can be completely accounted for in this way, while it still remains to be seen if all the excess conductance can be thus explained. The detailed discussion of this problem will be dealt with elsewhere in a general study of surface admittance.

SUMMARY

A method is described for determining surface conductance from observations on suspensions of spherical particles. Suspensions of glass and kaolin of diameters from 0.6 to 3.4μ in solutions of potassium chloride, hydrochloric acid and sodium carbonate have been studied at frequencies from 1/2 to 100 k.c. and the experimental surface conductances compared with the values calculated from a consideration of the diffuse double layer. The observed surface conductance can be accounted for on this basis only in part, the difference increasing as the frequency is increased (4). The existence of an additional type of current transport besides that offered by the diffuse double layer is also shown by the presence of surface capacitance (4), indicating a current transport (probably at the solid surface)

which is associated with polarization. There is a theoretical connection between the surface conductance and the surface capacitance (3) by which one can account for the frequency variation of the surface conductance.

REFERENCES

- (1) COLE: Cold Spring Harbor Symposia on Quantitative Biology 1, 23 (1933).
- (2) This method is due to F. G. Cottrell and C. G. Gilbert; compare BISHOP: Bur. Standards J. Research 12, 177 (1934).
- (3) FRICKE: Phil. Mag. 14, 310 (1932).
- (4) FRICKE AND CURTIS: Phys. Rev. 47, 529 (1935).
- (5) FRICKE AND CURTIS: Phys. Rev. 48, 775 (1935).
- (6) MAXWELL: Electricity and Magnetism, p. 313. The Clarendon Press, Oxford (1892).
- (7) MCBAIN AND FOSTER: J. Phys. Chem. 39, 331 (1935).
- (8) MÜLLER: Cold Spring Harbor Symposia on Quantitative Biology 1, 1 (1933).
- (9) SMOLUCHOWSKI: Physik. Z. 6, 529 (1905).
- (10) URBAN, WHITE, AND STRASSNER: J. Phys. Chem. 39, 311 (1935).

HYDROGEN BRIDGES IN ICE AND LIQUID WATER

MAURICE L. HUGGINS

Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland

Received March 19, 1936

It was shown by W. H. Bragg (3) in 1922 that the x-ray diffraction data obtained from ice by Dennison (4) were in agreement with a structure in which each oxygen is equidistant from four others tetrahedrally arranged around it.¹ This distribution of oxygens has since been verified by further work (1). Bragg proposed that, in agreement with the theory of "hydrogen bridges" (or "hydrogen bonds") proposed independently by the writer (5) and by Latimer and Rodebush (9), there is a hydrogen midway between each pair of adjacent oxygen atoms. Although the hydrogens do not contribute appreciably to the x-ray scattering, this seemed to be the most reasonable distribution, considering the symmetry of the arrangement of oxygens and the probable forces between the atoms.

That neighboring atoms in liquid water must be held together in very nearly the same way as in ice is indicated by the slight change of density, dielectric constant (2, 11), and various other properties on melting, by the low heat of fusion compared with the heat of vaporization, and by x-ray data obtained in this laboratory (8) and elsewhere (2) showing that on the average each oxygen in liquid water has about four neighboring oxygens at a distance only slightly greater than the O-O distance in the solid.

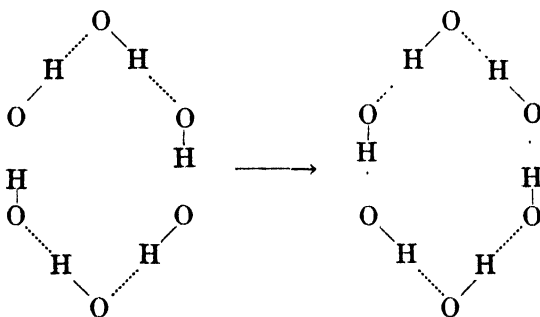
One is thus led to postulate hydrogen bridges throughout the liquid; many of these, however, being bent or stretched and some broken, at any instant, as a result of the heat motions. The bending of many of these bridges when ice melts permits a slightly closer packing, hence a greater density. As the temperature rises, more and more of the bridges are broken and stretched, the average interoxygen distance becomes larger, and the density decreases.

In several respects this picture has not been entirely satisfactory. The low conductivity of pure water compared with water containing hydrogen ions (and also negative ions, of course) seems quite inexplicable. Moreover the high dielectric constant in both the liquid and solid, down to temperatures considerably below zero (for low frequencies), seemed to be evidence for the existence of molecular units, some of which are quite free to orient themselves in an electrostatic field.

¹ A tetrahedral arrangement of four oxygens around each oxygen was predicted by the writer on the basis of the theory of hydrogen bridges.

Largely because of these two arguments the writer² suggested that the hydrogen of each hydrogen bridge in solid and liquid H_2O may be closer to one oxygen neighbor than to the other, in such a way that each oxygen keeps but two close hydrogen neighbors, all oxygens in ice and most of them in water also having two other hydrogen neighbors at a somewhat greater distance. As Pauling (10) has recently shown, this picture makes possible a calculation of the entropy of ice more nearly in agreement with experiment than that calculated on the assumption of rotating molecules. The additional assumption that the potential energy hump in the center of each hydrogen bridge in the structure is small is sufficient to account for both the conductivity and dielectric constant behavior, as will now be shown.

Although the shifting of a single hydrogen in a hydrogen bridge in ice or water from the vicinity of one oxygen to the vicinity of the other might be quite difficult, owing to the size of the energy hump, such a shift is much facilitated if at the same time another hydrogen nucleus approaches the first oxygen (thereby making its effective charge less negative) and a hydrogen previously close to the second oxygen moves away from it (making its effective charge more negative). Jumps in unison of all of the hydrogens in a ring, in such a way that after the jumps, as before, each oxygen has but two close hydrogen neighbors, may therefore occur quite frequently, just as a result of the ordinary heat energy.



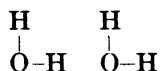
The presence of an external electrostatic field favors such jumping in all cases in which the resultant electric moment in the direction of the field is increased, hindering those jumps decreasing the electric moment in that direction. (For a 6-bridge ring the resultant moment change is

² In a preliminary edition of his book on "Chemistry, the Science of Atoms and their Interactions," in 1933. Essentially the same picture, as regards each atom's immediate neighbors, has been proposed by Bernal and Fowler (2).

slight; this is not so, however, for many larger, less symmetrical rings.) Qualitatively the effect is much the same as if the substance contained a small percentage of rotatable molecular dipoles, and the large dielectric constant in both solid and liquid is accounted for (cf. reference 2).

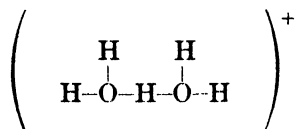
At temperatures which are too low, the temperature energy is insufficient to make even these synchronized shifts possible, and the dielectric constant decreases to a very small value. The shifts in a ring do not occur instantaneously as soon as the field is applied, as the vibrations of the atoms must be suitably timed and must have sufficient energy. Because of this time lag the dielectric constant values are less for high frequencies than for low frequencies, at any given temperature. When the temperature energy available is sufficiently large, the synchronized jumps of the hydrogens in a ring become synchronized oscillations about their mean positions. The effect of the field on this portion of the structure then becomes practically negligible. This accounts for the diminution of dielectric constant as the temperature rises, at temperatures slightly below zero, for low frequencies.

Each hydrogen nucleus in pure water may be considered, roughly, as bridging between an OH^- ion and an H_2O molecule. The bridge is obviously unsymmetrical, the hydrogen in question being held close to the OH^- (so producing an H_2O molecule):

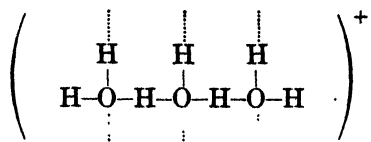


A jump of this hydrogen nucleus to the other end of the bridge, giving OH^- and H_3O^+ , practically never takes place (cf. figure 2); hence the extremely low conductivity of pure water.

If an acid is dissolved in water the hydrogen nuclei produced by dissociation undoubtedly also serve to bridge between oxygens, each such nucleus connecting two H_2O molecules. With less repulsion between the oxygens one would expect a shorter O-O distance than in the case just considered. The hydrogen would be expected to oscillate symmetrically about the midpoint. We may represent this situation thus:

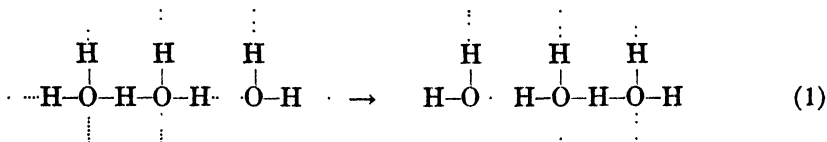


There is no *a priori* reason for eliminating the possibility of H_7O_3^+ and larger ions, containing two or more practically symmetrical bridges:



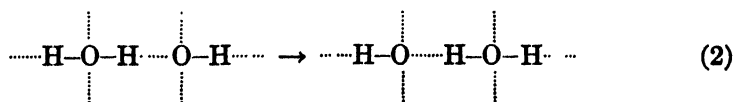
The larger such ions however, the less the stability of the symmetrical bridges; it seems likely that H_5O_2^+ is the usual limit.

The effective charge on each of the H_5O_2^+ oxygens is less negative than that on an H_2O oxygen. In view of this fact, we should expect such shifts as the following to occur readily:



In this process the charge shifts with but little actual motion of the atoms. In a potential gradient between two electrodes, shifts of this sort which move the positive charge toward the negative electrode are favored in preference to shifts in the opposite direction. As these shifts would be very rapid this theory accounts for the high mobility of hydrogen ion in water. (The chain mechanism postulated here differs but little from that proposed by the writer (6) in 1931. With the symmetrical bridges assumed at that time however, there was no obvious reason for the low conductivity of pure water, as noted above.)

In an OH^- ion the effective charge on the oxygen atom is more negative than on the oxygen atom in a water molecule, hence the O-H distance in this ion is less than in water. In water solution such an ion, unlike H^+ , would probably not form aggregates such as $(\text{H}-\text{O}-\text{H}-\text{O}-\text{H})^-$ because the larger Coulomb repulsion between the oxygens and larger Coulomb attraction between the central hydrogen and each oxygen would tend to make the central hydrogen bridge an unsymmetrical one. The oxygen atom in an OH^- ion would be expected to tend to surround itself with four unsymmetrical hydrogen bridges, like that in a water molecule or H_5O_2^+ ion. Shifts such as



would be expected to occur, although not so readily, on account of the greater O-O repulsion, as shifts of the type of equation 1. It is thus

reasonable that the mobility of the hydroxide ion is greater than that of other ions which cannot exchange atoms with the solvent in this way, and still is less than that of hydrogen ion.

In attempting to make the treatment of hydrogen bridges in ice and water more quantitative, we shall first consider a hypothetical bridge in which the energy of interaction between neighboring hydrogen and oxygen atoms is the same as in the OH molecule in its normal state. (Many of the calculations have also been carried out using the constants for a higher energy state, with results only slightly different from those to be described.) For this interaction we assume a modified Morse function, of the type recently applied successfully by the writer (7) to the calculation of molecular constants for diatomic molecules. This is of the form

$$U \text{ (in } 10^{-12} \text{ ergs)} = e^{-a(r-r_{12})} - C'e^{-a'(r-r_e)} \quad (3)$$

in which a , a' , r_{12} and C' are constants determined from band spectrum data. In this case $a = 6.0$, $a' = 1.29$, $r_{12} = 1.125$ (assumed to be the same as calculated for the $^2\Sigma^+$ state) and $C' = 11.83$. The equilibrium distance r_e is 0.969. For the method of calculating the other constants from a , r_{12} , r_e and the vibration frequency ω_1 , the writer's first paper (7) on diatomic molecules may be consulted.

Taking the oxygen to oxygen distance as 2.75 A.U. (its value in ice), the potential energy, for a hydrogen moving along the O-O centerline, changes as shown in the top curve of figure 1. It is seen that there are two minima, about 1.10 A.U. from the oxygens, with an energy hump between them of about 0.15×10^{-12} erg. It may be noted that $\frac{1}{2} kT$, the average molecular energy per degree of freedom, is only about 0.02×10^{-12} erg at room temperature. If the O-O distance is taken as 2.70 A.U., the experimental value for hydrogen bridges in H_3BO_3 , $AlHO_2$ and some other compounds, the size of the central hump is very much diminished and the shorter O-H distance is increased to 1.13 A.U. For a distance between oxygens of 2.55 A.U., such as observed in $NaHCO_3$ and KH_2PO_4 , there is but one minimum, at the center.

From these results one must conclude that, if our assumption regarding the variation of the O-H interaction energy with distance is even approximately correct, the hydrogen bridges in ice and liquid water cannot be symmetrical, with the hydrogens oscillating about points midway between the oxygens. Each hydrogen must remain considerably closer to one oxygen neighbor than to the other.

It is obvious that the energy is lowest—the stability greatest—if each oxygen in ice or liquid water has two close hydrogen neighbors. The effective charge on the oxygen of an H_3O^+ ion is less negative and that on the oxygen of an OH^- ion is more negative than that on an oxygen of an

H_2O molecule. The attraction between the oxygen of an H_3O^+ ion and each of its hydrogens is therefore less than that between an H_2O oxygen and each of its hydrogens; likewise the attraction between the two atoms of an OH^- ion is greater. Calculation shows that a very slight difference in effective charge on the two oxygens joined by a hydrogen bridge suffices to eliminate the double hump in the potential energy curve, leaving only a

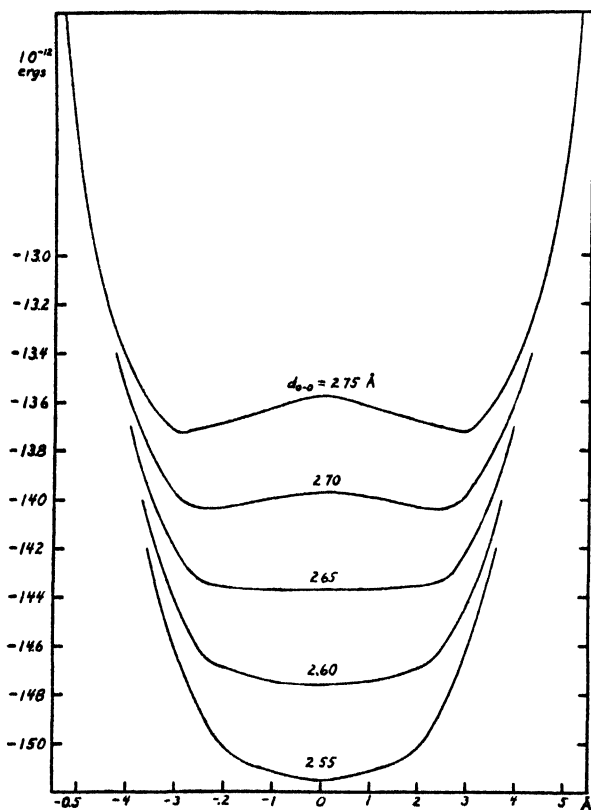


FIG. 1. Potential energy curves for hydrogen bridges with various fixed oxygen-oxygen distances, assuming the O-H interactions to vary with distance as in the OH molecule.

single minimum on the side of the oxygen with the more negative effective charge. Adding to the O-H interaction energy represented by the uppermost curve of figure 1 a term $\alpha e^2/d_{\text{H-O}}$, to take account of a decreased Coulomb attraction between the hydrogen atom and one of the oxygens, unsymmetrical single-minimum curves (see the two lowest curves of figure 2) are obtained for all values of α greater than $1/20$ (for $d_{\text{O-O}} = 2.75$ A.U.). If at the same time another term of the same form but opposite sign to

represent an increased attraction between the hydrogen and O_2 is included, the central hump is eliminated with still smaller values of α . One must conclude then that a shift of one hydrogen of an H_2O molecule to a neighboring molecule to give H_3O^+ and OH^- ions could not occur.

If one decreases the effective negative charge equally on both oxygens of a hydrogen bridge, the central hump tends to disappear, both because of a

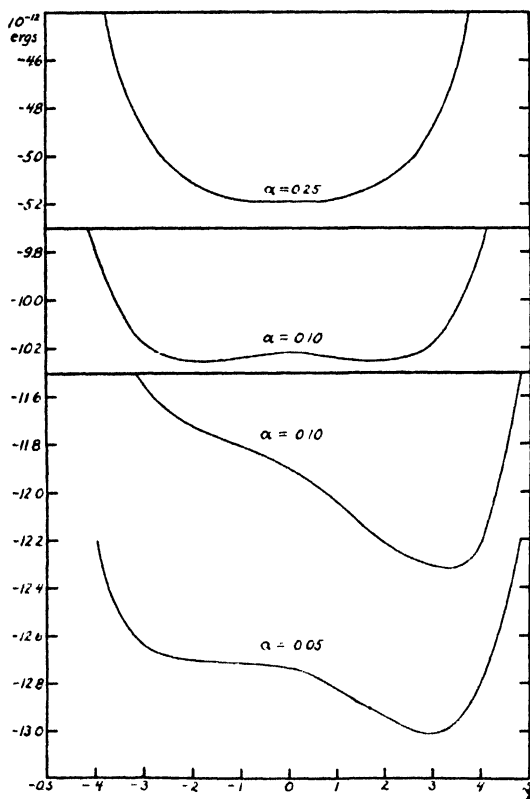


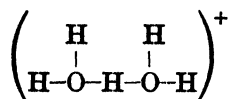
FIG. 2. Potential energy curves for hydrogen bridges having d_{O-O} fixed at 2.75 A.U. To the O-H interaction energy as in the OH molecule a Coulomb term $\alpha e^2/d_{O_1-H}$ is added for each of the two lowest curves. For the two others terms of this form are added for both O_1-H and O_2-H interactions.

decrease in the O-O distance (figure 1) and because of the decreased Coulomb attraction between the hydrogen and each oxygen (see the two upper curves of figure 2). This furnishes the justification for the assumption that the hydrogen ion consists of a relatively strong, symmetrical bridge joining two H_2O groups. Reversing the argument, a hydrogen bridge connecting two OH^- ions would be weaker, longer, and more un-

symmetrical than the bridges in pure water (connecting, in effect, OH⁻ ions and H₂O molecules).

As will be shown elsewhere, the F-F distance in the FHF bridge can be calculated with reasonable accuracy, using constants obtained entirely from other sources. To a large extent this distance depends on the interpenetration repulsion between the two fluorine atoms, assumed to be representable by an exponential term, $e^{-a(r-r_{12})}$. Because of inaccurate knowledge of the best value of r_{12} to use for the repulsion between two oxygen atoms, of the effective charges on the oxygen and hydrogen atoms, and of the magnitudes of the van der Waals constants, the corresponding calculation for OHO bridges cannot at present be carried out satisfactorily. It is instructive however to calculate the value of r_{12} which is necessary to give equilibrium for different O-O distances, neglecting the van der Waals terms (which are small) and the Coulomb terms (which do not change rapidly with the distance). Taking $a = 4.78$ as for neon and fluorine, one obtains $r_{12} = 2.80$ for $d_{oo} = 2.75$ A.U. and $d_{o,H} = 1.10$ A.U. For O-O and O₁-H distances of 2.70 A.U. and 1.13 A.U., respectively, $r_{oo} = 2.78$ A.U. For $d_{oo} = 2.55$ A.U., with the hydrogen in the middle, $r_{oo} = 2.70$ A.U. It is seen that a small decrease in the "basic radius" ($r_o = r_{oo}/2$) suffices to change an unsymmetrical bridge (two minima in the potential curve) into a symmetrical one (only one minimum, in the middle). This "radius" is a measure of the extension in space of the outermost electrons in the atom *in the direction of the other oxygen*. Its value depends on the tightness with which these electrons are held by the kernel and on what is on the other side—on the polarizability of the atom and on the magnitudes and directions of the forces tending to polarize it.

Increased polarization resulting in a decreased basic radius for the oxygen at each end of a hydrogen bridge—and so a decreased O-O distance—may result from an increase in the number of close hydrogens or from their replacement by atoms of a sufficiently electronegative element such as carbon or phosphorus. In either case a single minimum potential curve is favored. This line of reasoning furnishes an additional argument for the structure



with a strong central bridge, for the hydrogen ion in water solution. It also accounts for the small O-O distances observed in sodium bicarbonate and potassium dihydrogen phosphate.

SUMMARY

Evidence for the existence of hydrogen bridges in liquid and solid water and against their being symmetrical is reviewed. With sufficiently small

energy barriers in the center of each OHO bridge, synchronized jumps over them of all of the hydrogens in a ring of hydrogen bridges are possible. The resulting partial freedom of orientation of the dipoles accounts satisfactorily for the dielectric constant data for ice and liquid water. Reasons are given for considering hydrogen ion in water to be $(\text{H}_2\text{OHOH}_2)^+$, consisting of a relatively strong, symmetrical hydrogen bridge connecting two H_2O groups. By very slight contemporaneous shifts of two hydrogen nuclei, such an ion can, in effect, add OH_2 at one end and lose H_2O at the other, thus shifting the position in the solution of the excess positive charge. This picture thus accounts for the high mobility of the hydrogen ion in water solution.

Potential energy curves for OHO bridges are calculated for different O—O distances, taking the O—H interactions as in the OH molecule. For the smaller distances there is a single potential minimum; for the larger distances, such as observed in liquid and solid water, it is double. The central hump is eliminated if the Coulomb attraction between the hydrogen and one or both of the oxygens is slightly greater than in the OH molecule.

The hydroxide ion is probably OH^- rather than $(\text{HOHOH})^-$, the greater repulsion between the oxygen atoms making a symmetrical bridge less likely than in the case of the positive ion. The shift $\text{H—O—H} \dots \text{O—H}$ to $\text{H—O} \dots \text{H—O—H}$ should occur, but less readily than the corresponding shift in the case of hydrogen ion, hence the mobility should be less, as observed.

REFERENCES

- (1) BARNES, W. H.: *Proc. Roy. Soc. London* **125A**, 670 (1929).
- (2) BERNAL, J. D., AND FOWLER, R. H.: *J. Chem. Physics* **1**, 515 (1933).
- (3) BRAGG, W. H.: *Proc. Phys. Soc.* **34**, 98 (1922).
- (4) DENNISON, D. M.: *Phys. Rev.* **17**, 20 (1921).
- (5) HUGGINS, M. L.: Undergraduate thesis (1919).
- (6) HUGGINS, M. L.: *J. Am. Chem. Soc.* **53**, 3190 (1931).
- (7) HUGGINS, M. L.: *J. Chem. Physics* **3**, 473 (1935); also another article in press.
- (8) KATZOFF, S.: *J. Chem. Physics* **2**, 841 (1934).
- (9) LATIMER, W. M., AND RODEBUSH, W. H.: *J. Am. Chem. Soc.* **42**, 1419 (1920).
- (10) PAULING, L.: *J. Am. Chem. Soc.* **57**, 2680 (1935).
- (11) SMYTH, C. P., AND HITCHCOCK, C. S.: *J. Am. Chem. Soc.* **54**, 4631 (1932).

THE DIFFUSION OF COPPER SULFATE IN AQUEOUS SOLUTIONS OF SULFURIC ACID

A. F. W. COLE AND A. R. GORDON

Chemistry Department, University of Toronto, Toronto, Canada

Received August, 1935

For an electrochemical problem now being investigated in this laboratory, it was necessary to know the diffusion constant of copper sulfate in aqueous solution in the presence of varying amounts of sulfuric acid. A search of the literature showed that the complaints of other investigators as to the meagerness and uncertainty of the diffusion data would have been justified in the case of copper sulfate also. We have therefore determined the diffusion constant of copper sulfate in aqueous solutions of sulfuric acid, and the results are recorded here.

The method was that originally developed by Northrup and Anson (4) and since that time used extensively by McBain and his associates (3); since it has already been discussed adequately in the literature, no lengthy description is needed. In brief, it consists in enclosing in a glass cell of known volume a solution of the material whose diffusion constant is desired; the base of the cell is a sintered glass diaphragm whose pores are sufficiently small to prevent streaming of the solution as a whole, and at the same time are large enough to permit diffusion to take place unhindered. The cell is suspended with the diaphragm just dipping below the surface of an equal volume of pure solvent, and after allowing diffusion to proceed for a suitable length of time, the amount of solute that has diffused through the diaphragm is determined; from this it is possible to compute the diffusion constant, provided the cell has previously been calibrated with a substance of known diffusion constant.

It has been found desirable, after filling the cell with solution, to carry out a preliminary diffusion to ensure a more or less linear drop of concentration in the diaphragm before transferring the cell to the sample of solvent into which the final diffusion is to take place. Under these conditions, it can easily be shown, on the assumption that Fick's diffusion law is obeyed, that to a first approximation

$$\begin{aligned}c' &= \frac{c_0}{2} (1 + e^{-2kAt/lV}) \\c'' &= \frac{c_0}{2} (1 - e^{-2kAt/lV})\end{aligned}\tag{1}$$

where c_0 is the initial concentration inside the cell in equivalents per liter, c' and c'' are the concentrations of the inner and outer solutions after the diffusion has proceeded for t seconds, A and l are the effective cross-sectional area and thickness of the diaphragm, and V is the volume of both the inner and outer solutions. Hence

$$\beta kt = \log (c' + c'') - \log (c' - c'') \quad (2)$$

where β , the "cell constant," is $2A/2.3026 lV$, and can be determined once and for all for the cell by diffusion measurements with a substance of known k .

The use of equations 1 and 2 involves the assumption (in addition to that implicit in Fick's law) that the concentrations of the inner and outer solutions are changing so slowly that a steady state is set up in the diaphragm, i.e., that there is a linear drop of concentration throughout the diaphragm at all stages of the experiment. Actually, as Barnes (1) has shown, this is not necessarily the case, but he finds from a rigorous solution of the problem, that to a high order of approximation the only change introduced in equations 1 and 2 is that β becomes $(2A/2.3026 lV) \times (1 - \lambda/6)$, where λ is the ratio of the volume of the liquid in the diaphragm to that in the cell. Since this revised cell constant depends only on the geometry of the apparatus and is determined automatically by the calibration, no error is introduced by this cause in equation 2.

The assumption of Fick's law, however, implying that k is independent of c , is a more serious matter. If k does depend on the concentration, the concentration gradient $\partial c/\partial x$ will vary from top to bottom of the diffusion layer even when a steady state has been attained in the diaphragm. However, on the assumption that $k = k_0 (1 - \alpha c)$, which fortunately covers the case of copper sulfate, it is easy to allow for this. At any cross section of the diaphragm, the total amount diffusing in a time dt is $-kA(\partial c/\partial x)dt$, which, for a steady state in the diaphragm, is constant from the upper surface of the diffusion layer ($x = 0$) to the lower surface ($x = l$). Assume an "effective" diffusion constant k' , independent of c , which will cause the same amount of solute to diffuse for the same total drop in concentration across the diaphragm. Then

$$-k'A \frac{(c'' - c')}{l} \cdot dt = -kA \cdot \frac{\partial c}{\partial x} \cdot dt \quad (3)$$

Simplifying, multiplying through by dx , and integrating between the limits $x = 0$ and $x = l$,

$$k'(c' - c'') = - \int_0^l k \cdot \frac{\partial c}{\partial x} \cdot dx = k_0 \int_{c''}^{c'} (1 - \alpha c) dc \quad (4)$$

Hence

$$k' = k_0 - k_0\alpha(c' + c'')/2$$

but $(c' + c'')$ is constant throughout the experiment. Therefore the "effective" diffusion constant, k' , computed by equation 2 is the true (differential) diffusion constant for the average of the inside and outside concentrations, or (what is the same thing) for one-half the initial inside concentration.

The cells used were similar to those employed by McBain,—of Jena glass with G4 pore size and of about 100-cc. capacity. Their volumes were determined by weighing the cell with liquid just to the top of the diaphragm, and then weighing again when full; the volumes so determined could be checked to 0.1 cc. The liquid in the outer compartments (small beakers of 125-cc. capacity) was measured by specially calibrated pipets. During a measurement, each cell with its attendant beaker was suspended in an individual glass air bath immersed in a water thermostat electrically controlled to $\pm 0.02^\circ\text{C}$. The cells and beakers were carried by a bridge which had no connection with the thermostat and which was supported on sponge rubber blocks to minimize vibration; each cell was hung from a wire suspension to ensure that the diaphragm was horizontal, and this suspension and the support for the beaker forming the outside compartment were attached to ebonite rods to avoid any transfer of heat from the outside air to the solutions.¹ The top of each air bath was closed with a slotted fiber disk covered with absorbent cotton, and as an additional precaution against evaporation from the outside compartment, a few cubic centimeters of a solution roughly isotonic with that in the outer compartment were placed in the bottom of each air bath.

The cell constants were determined by calibration at 20°C . with $N/10$ potassium chloride solution, whose diffusion constant has been found by Cohen and Bruins (2) to be $1.448 \text{ cm.}^2 \text{ per day} = 1.676 \times 10^{-5} \text{ cm.}^2 \text{ per second}$; successive calibrations for a cell gave values of β differing in general by less than one fifth of 1 per cent.

The acid copper sulfate solutions with which the cells were initially filled were made up from recrystallized B.D.H. analytical reagent copper sulfate, a stock solution of c.p. sulfuric acid, and boiled conductivity water; the sulfuric acid solution which was to be placed in the outer compartment was always made up to the same volume concentration of acid as the solution to be used in the cell. After a preliminary diffusion to set up a steady

¹ We have found that to obtain consistent results it was necessary to eliminate vibration as far as possible, and also to control temperature somewhat more carefully than has been suggested by other investigators; a fluctuating temperature produces a pumping action of the solution in the cell which tends to break up the diffusion layer in the diaphragm.

state in the diaphragm (usually with copper sulfate solutions this required ten to twelve hours), the cell and beaker (now containing a fresh sample of

TABLE 1
Data for run No. 175
Acid concentration = 3.6 equivalents per liter; $T = 18.00^{\circ}\text{C}.$;
 $t = 125.62 \text{ hours} = 4.522 \times 10^6 \text{ sec.}$

CELL	β	c'	c''	$k \times 10^6$
Cell II.....	0.0777	0 5208	0 1016	4 89
Cell III.....	0 0826	0 5162	0.1072	4 90
Cell IV.....	0 0549	0 5496	0 0763	4 88
Cell V.....	0 0654	0 5379	0.0883	4.87

TABLE 2
Values of k_0 and of $k_0\alpha$

Equivalent H_2SO_4 per liter.....	0	0 005	0 10	0 10	0 10	0.5	1 0	3.6	7 6
$T^{\circ}\text{C}.$	18	18	10	18	25	18	18	18	18
$10^6 \cdot k_0$	6 28	6.28	4 97	6 28	7 81	6 24	6 01	5 02	3 66
$10^6 \cdot k_0\alpha$	2 56	2 56	2 00	1 60	2 70	0.94	0 82	0 32	0 12

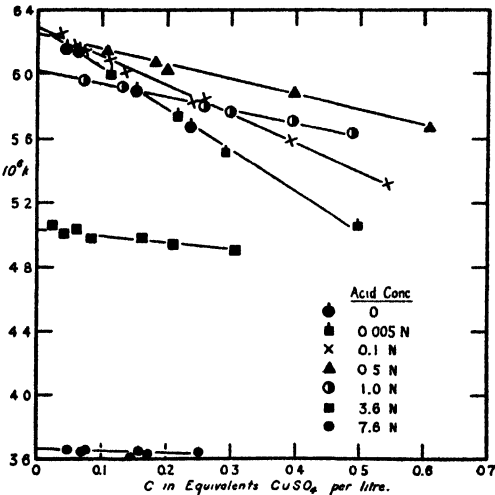


FIG. 1. The diffusion of copper sulfate in aqueous solutions of sulfuric acid at $18^{\circ}\text{C}.$

the acid solution) were left in the thermostat for from five to eight days; at the end of this time, the cell was removed from the beaker, and both solutions were analyzed electrolytically for copper. As an example, the

data for one such run, selected at random, are summarized in table 1. Thus from the table, the diffusion constant of copper sulfate in a solution containing in 1 liter 3.6 equivalents of sulfuric acid and 0.31 equivalent of copper sulfate is 4.89×10^{-6} cm.² per second.

The results of a large number of such measurements, all at 18°C., are shown in figure 1; each point is the average of four measurements similar to those recorded in table 1. It is evident from the graph that for a given acid concentration and for the range of copper concentrations used, k is a linear function of c to a close approximation. Table 2 gives the values of k_0 and of $k_0\alpha$ for various strengths of acid, and also for various temperatures for one acid concentration.

It is evident from the table that for solutions extremely dilute in copper sulfate the diffusion constant decreases in a more or less linear manner with increasing acid concentration. Since the forces retarding diffusion are usually assumed to be proportional to the viscosity, one would expect that the product $k_0\eta$ for a given temperature would be roughly constant, and this is very approximately the case.² In the more concentrated solutions, however, increase in acid concentration tends to decrease the dependence of k on the copper concentration, and at the moment there does not seem to be any plausible explanation of this.

We have also carried out a few experiments to measure any diffusion of the sulfuric acid during an experiment. Naturally this will only be prominent if the acid concentration is relatively small, and the difficulties of analysis (barium sulfate precipitation in the presence of a copper salt) are considerable. However, our results show, as might be expected, a definite diffusion of the acid from the outer solution to the inner, i.e., against the copper sulfate; thus in one experiment ($c_0 = 1.6312$, $c' = 1.3200$, $c'' = 0.3122$ equivalent of copper sulfate per liter) with 0.1 N sulfuric acid as solvent, it was found after one hundred and ninety-two hours diffusion that the inner solution was 0.014 equivalent of sulfuric acid per liter stronger than the outer. On the other hand, with relatively high concentrations of acid (1 N or more), there is evidence of a slight but definite diffusion of acid with the copper; this effect is now being investigated in this laboratory.

REFERENCES

- (1) BARNES: *Physics* **5**, 4 (1934).
- (2) COHEN AND BRUINS: *Z. physik. Chem.* **103**, 349 (1923); **113**, 157 (1924).
- (3) MCBAIN AND LIU: *J. Am. Chem. Soc.* **53**, 59 (1931).
- MCBAIN AND DAWSON: *J. Am. Chem. Soc.* **56**, 52, 1021 (1934); *Proc. Roy. Soc. London* **148A**, 32 (1935).
- (4) NORTHRUP AND ANSON: *J. Gen. Physiol.* **12**, 543 (1929).

² The product $k_0\eta$ increases about 15 per cent when the acid concentration increases from 0.1 N to 7.6 N .

A PRELIMINARY STUDY OF THE ABSORPTION SPECTRA OF CEPHALIN, LECITHIN, AND SELECTED ANTIGENS¹

AUGUSTUS WADSWORTH AND M. O'L. CROWE

*The Division of Laboratories and Research, New York State Department of Health,
Albany, New York*

Received March 27, 1936

Additional data on the antigens which are used in the complement-fixation and precipitation tests for syphilis are essential for comparative purposes and for determining the relationship between the antigenicity of these substances and their physical and chemical characteristics and, ultimately, in a comprehensive search for the antigenic substance which is responsible for the serological reactions of syphilis. Hence, a quantitative spectrophotometric study of cephalin and lecithin from beef brain in different stages of purification and of beef-heart antigens prepared in this laboratory for routine use in the serological tests for syphilis, and for experimental purposes, has been undertaken; the preliminary work is here reported.

The observations recorded are based on a study of the absorption spectra of these materials in the visible and ultra-violet ranges between λ 6800 and 2150 A.U.

Absorption spectrum curves in the visible region were obtained with a Hilger-Nutting spectrophotometer with a Pointolite lamp of 150-candle power as light source. The wave-length drum of the spectrophotometer was calibrated by means of a mercury arc and by helium, nitrogen, and hydrogen-discharge-tube spectra. The position of the prism was checked before making each set of readings by adjusting the position of the yellow line of helium, λ 5876 A.U. For the determination of the density values in the regions where the materials were particularly transparent, a neutral filter was used, and the cells containing the absorbing substance and the control were interchanged. In all cases at each wave length, density values obtained with the spectrophotometer and used in the calculation of the extinction coefficients are based upon at least five determinations.

The absorption spectrograms for the ultra-violet region were obtained with a Hilger E 316 quartz spectrograph used in conjunction with a Hilger sector photometer. The wave-length scale of the quartz spectrograph was calibrated with mercury-arc, aluminum-spark, helium-tube, and hydro-

¹ Presented at the meeting of the Society of American Bacteriologists, held in New York, December 28, 1935.

gen-discharge-tube spectra. The light source was a tungsten-steel condensed spark.

The accuracy of the spectrophotometric technic was tested in the visible region by comparison of curves obtained for copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) and potassium dichromate solutions in different cell depths with the standard curves for these substances published by Mecke and Ley (3), Houstoun (2), Grünbaum (1), and others. In the ultra-violet region the spectroscopic procedure was tested by a comparison of curves for potassium dichromate with the standard curves for this substance recorded by von Halban and Siedentopf (6), Rössler (5), and others. The agreement between all the standard curves and ours was very close.

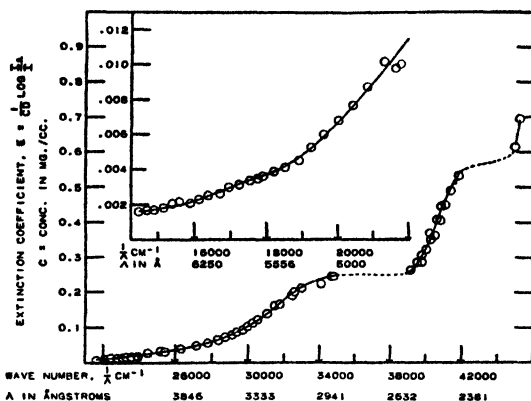


FIG. 1. Visible and ultra-violet absorption spectrum curves of purified cephalin from beef brain

All the solutions studied were apparently clear, yet faint Tyndall light, manifesting scattering of light, was observed; but the correction of the absorption curves for this effect has not yet been determined.

Purified cephalin, for which published data are given by Wadsworth, Maltaner, and Maltaner (8, 9), and lecithin, not highly purified, were investigated by this method. The antigens studied were those used in the routine complement-fixation tests for syphilis, which are modifications of the Bordet-Ruelens and of the Neymann-Gager type, and those prepared for precipitation tests by a new method (7).

The absorption spectrum curve for purified cephalin is presented in figure 1. Wave lengths in Ångström units and wave numbers, $\frac{1}{\lambda}$ cm.⁻¹, are plotted against extinction coefficient,

$$E = \frac{1}{cd} \log \frac{I_0}{I}$$

where c is the concentration in milligrams per cubic centimeter, d is the depth of the cell—in this case, 1 cm.— I_0 is the intensity of incident light, and I is the intensity of light after passing through the solution.

The curve for cephalin is fairly smooth in the visible region, with a slight change in slope between λ 6250 and 5550 A.U., but in the ultra-violet range it indicates two regions where inflections occur: one between λ 2850 and 2550 A.U., E about 0.25, near where the proteins are known to absorb radiation, and a second between λ 2400 and 2220 A.U., where E is about 0.55.

A previous very limited study of lecithin, not highly purified, yielded an absorption curve in the visible region of the spectrum which was smooth and indicated very little absorption between λ 7000 and 5000 A.U., where the absorption began to increase. Spectrograms for the ultra-violet

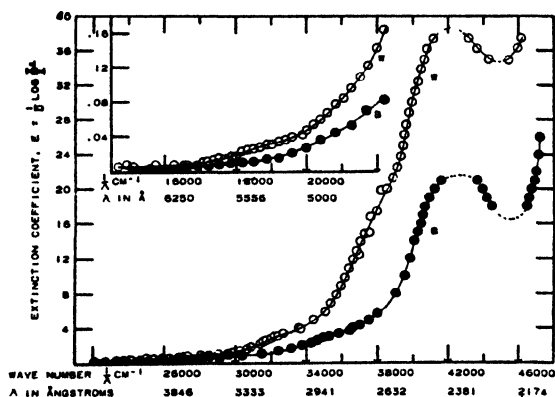


FIG. 2. Comparison of the visible and ultra-violet absorption spectrum curves of beef-heart antigens for complement-fixation tests prepared by modified methods of Bordet and Ruelens (curve B) and Neymann-Gager (curve W).

region gave evidence of selective absorption between λ 2800 and 2500 A.U. and between λ 2400 and 2230 A.U. These two regions occur about where selective absorption was indicated by the ultra-violet absorption curves for cephalin.

The absorption curves for one sample each of a modified Bordet-Ruelens and of a modification of a Neymann-Gager antigen are presented in figure 2. In the preparation of the Bordet-Ruelens antigen, the acetone-extracted tissue was further thoroughly extracted with anhydrous ether. The vacuum-dried tissue was then extracted with absolute alcohol at room temperature for ten days. The filtered extract is the antigen used for curve B. The modification of the Neymann-Gager antigen, which is represented by curve W, employs air-dried tissue, preliminary extraction with anhydrous ether, and final extraction by boiling with absolute alcohol.

Curve W represents a substance which is less transparent in both the visible and ultra-violet ranges of the spectrum than that represented by curve B. Both curves are fairly smooth in the visible region, with a slight inflection within the range from λ 5450 to 5300 A.U. in curve W. The latter also shows inflections within the range of about λ 3350 to 2950 A.U. and λ 2850 to 2530 A.U., where curve B is smooth. Both curves have definite absorption bands farther in the ultra-violet. The maximum of this band for curve W is at λ 2375 A.U., where the extinction coefficient ($E = \frac{1}{d} \log \frac{I_0}{I}$) is $38.4 \pm$; the minimum, at λ 2235 A.U., where E is $34.5 \pm$.

The maximum of the band in curve B lies about 40 A.U. farther towards the shorter wave lengths—that is, at λ 2335 A.U., where the extinction coefficient is $21.8 \pm$; the minimum at λ 2190 A.U., where E is $16.5 \pm$.

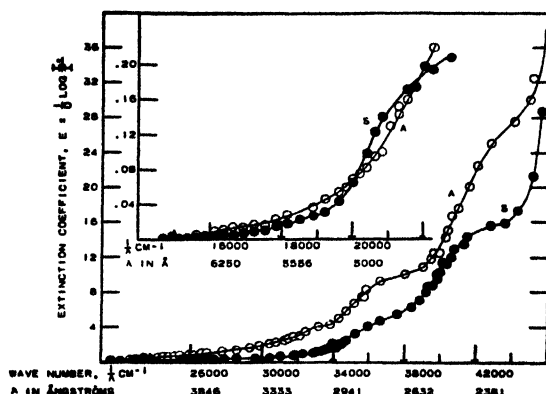


FIG. 3. Comparison of the visible and ultra-violet absorption spectrum curves of beef-heart antigens for precipitation tests prepared from tissue infused with water (curve A) and with 20 per cent sodium chloride solution (curve S).

The hydrogen-ion concentration values, determined colorimetrically, were the same for all the antigens for which absorption curves are presented.

The antigen represented by curve A in figure 3 was prepared for use in a precipitation test. It was a 95 per cent alcoholic extract of beef-heart tissue which had been subjected to an aqueous infusion at 55°C., previous to acetone treatment and subsequent drying. The antigen represented by curve S was a 95 per cent alcoholic extract of tissue similarly treated, except that the infusion was carried out with a 20 per cent sodium chloride solution in place of water.

A comparison of their absorption curves in the visible range of the spectrum shows that the antigen which is prepared from tissue treated with sodium chloride solution shows an inflection in its curve S in the range of

λ 4950 to 4600 A.U. whereas the curve A for the antigen prepared from tissue infused with water shows no inflection in this range. Both curves indicate little absorption in the range λ 6800 to 5500 A.U., in which curve A represents slightly higher values of extinction coefficient than curve S. This work has been further substantiated by determining the curves for two other antigens of the same type, prepared in the same way as the antigens represented by curves A and S.

In the ultra-violet range between λ 4160 and 3900 A.U., curve S shows indications of selective absorption, whereas curve A is smooth. This difference is more clearly indicated in figure 4. Both curves have inflections in the ranges from λ 2800 to 2600 A.U. and from λ 2500 to 2300 A.U., approximately. Curve A has a slight inflection near λ 3000 A.U. and represents

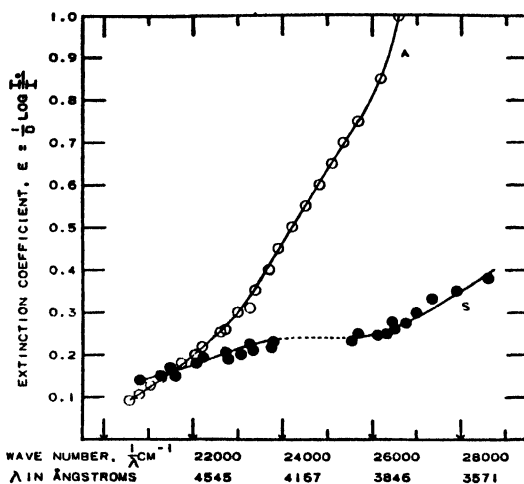


FIG. 4. Comparison of absorption spectrum curves of beef-heart antigens A and S within the range λ 4800 to 3700 A.U.

a less transparent substance than does curve S throughout the ultra-violet range of the spectrum. In order to illustrate more clearly than is indicated in figure 3 the contrast in the curves in the range between λ 4160 and 3900 A.U., this portion of the curves has been drawn to a much more open scale and is presented in figure 4. The flat portion of curve S is contrasted with the smooth portion of curve A in this range.

Curves for each of the two types of antigens—complement fixing and precipitating—which have already been shown in figures 2 and 3, have been plotted together for comparative purposes and are presented in figure 5.

There are a number of points of difference between the curves W and S for the complement-fixation and precipitation antigens, respectively, but

the most outstanding difference is within the range from λ 2500 to 2300 A.U., where the curve W shows a definite absorption band (E value for maximum, $38.4 \pm$), whereas curve S has merely an inflection and indicates less absorption, with values for E between 10 and 15.8 within this range. Curves for several other antigens showed definite bands for the complement fixation, and inflections only for the precipitation types. Curve W indicates selective absorption in the ultra-violet ranges from λ 3350 to 2950 A.U. and from λ 2850 to 2530 A.U., and is fairly smooth in the visible region of the spectrum. Curve S has slight inflections between λ 2800 and 2600 A.U. and λ 2500 and 2300 A.U. in the ultra-violet and a definite inflection in the visible region from λ 4950 to 4600 A.U., where the curve W is smooth and indicates less absorption.

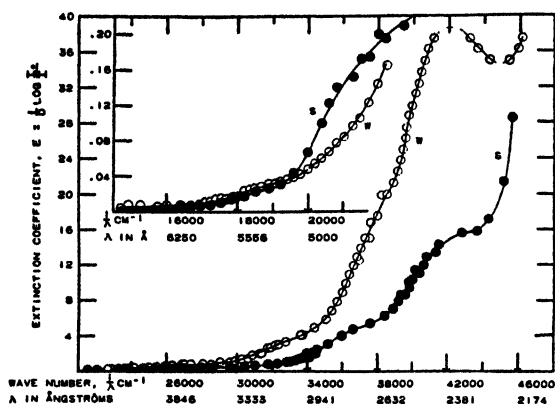


Fig. 5. Comparison of the visible and ultra-violet absorption spectrum curves of a modified Neymann-Gager antigen (curve W) and one for precipitation tests prepared from tissue infused with 20 per cent sodium chloride solution (curve S).

It seems well to record here a supplementary note regarding the fluorescence of these materials and also of the results of tests for the effects of exposure to ultra-violet radiation. All of the substances for which absorption curves have been shown fluoresced when irradiated with ultra-violet light from either a carbon arc or a quartz mercury-vapor arc through a Corning red-purple corex filter. Solutions of cephalin are generally characterized by fluorescence, according to Parnas (4). The sample studied fluoresced with a brilliant blue light, the band extending from about λ 6300 to 4200 A.U., the maximum intensity being between λ 5300 and 5200 A.U.; all the antigens fluoresced with a bluish-green light. There was no significant change in the coagulative activity of cephalin which had been exposed to the ultra-violet light of the tungsten-steel condensed spark for the time required to make spectrograms, nor in the degree of fixation

of complement obtained in antigen or antibody titrations performed with syphilitic sera and the antigens represented by curves B and W.

SUMMARY

From this preliminary spectroscopic study of cephalin, lecithin, and beef-heart antigens, it is noted that selective absorption in two ranges of the ultra-violet regions of the spectrum, about λ 2850 to 2500 A.U. and λ 2550 to 2200 A.U., is common to all and that the first range is near that in which the proteins are known to absorb. Differences between the absorption curves for the complement-fixation and precipitation antigens and between two samples of each type have also been recorded.

Little consideration has as yet been given to the identification of the substances which may be responsible for the selective absorption indicated by the curves shown.

REFERENCES

- (1) GRÜNBAUM, F.: *Ann. Physik* **317**, 1004 (1903).
- (2) HOUSTOUN, R. A.: *Proc. Roy. Soc. Edinburgh* **32**, 40 (1912).
- (3) MECKE, R., AND LEY, H.: *Z. physik. Chem.* **111**, 385 (1924).
- (4) PARNAS, J.: *Biochem. Z.* **22**, 411 (1909), cited by Hugh Maclean and Ida S. Maclean in "Lecithin and Allied Substances; the Lipins," 2nd edition, p. 54. Longmans, Green and Co., Ltd., New York (1927).
- (5) RÖSSLER, G.: *Ber.* **59**, 2609 (1926).
- (6) VON HALBAN, H., AND SIEDENTOPF, K.: *Z. physik. Chem.* **100**, 208 (1922).
- (7) WADSWORTH, AUGUSTUS, AND BROWN, RACHEL: *J. Bact.* **31**, 72 (1936).
- (8) WADSWORTH, AUGUSTUS, MALTANER, FRANK, AND MALTANER, ELIZABETH: *Am. J. Physiol.* **97**, 74 (1931).
- (9) WADSWORTH, AUGUSTUS, MALTANER, ELIZABETH, AND MALTANER, FRANK: *J. Immunol.* **26**, 25 (1934).

A STUDY OF THE LAWS GOVERNING THE CATION-EXCHANGING PROPERTIES OF A PRECIPITATED ALUMINUM SILICATE

R. CHARLES BACON

The Royal Veterinary and Agricultural College, Copenhagen, Denmark

Received November 21, 1935

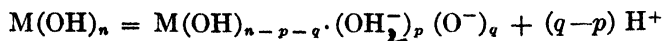
INTRODUCTION

Upon undertaking (1) the research here described, it was the intention of the author to study the quantitative variation in certain properties, especially that of cation exchange, as a function of the composition of a precipitated aluminum silicate. However, this proved to require considerable preliminary work, since it was found that the factors upon which the cation-exchange capacity depended were not sufficiently known. That is to say, the cation-exchange capacity depends on so many variables that it was found necessary to study a particular case first.

It was decided to prepare an aluminum silicate under known conditions, then to measure a series of properties for it. In this paper the theoretical aspects of the aluminum silicate considered as a colloidal particle will be taken up first. This will be followed by the experimental results.

THEORETICAL

Let us first consider the picture of the suspended particle (2). We may suppose the particle to consist of an interlacing of aluminum and silicon by oxygen atoms in a more or less random manner.¹ Further, the particle contains a number of hydroxyl groups attached either to silicon or aluminum atoms. We may assume that these hydroxyl groups are capable of splitting off hydrogen ions or of taking up hydrogen ions. That is to say, a negative or positive charge may be produced at a given point on the surface of the particle, according to whether we have respectively an ionization by the splitting off of a hydrogen ion or the acceptance of such an ion from the solution. To a varying degree according to the conditions, these two processes take place in each particle. This may be represented schematically in some such way:



¹ That this arrangement is random is indicated by the fact that no lines were found on a Röntgen photograph of our precipitate.

Where $M(OH)_n$ represents the unionized particle with n OH groups, and $M(OH)_{n-p-q} \cdot (OH_2^+)_p (O^-)_q$ the ionized form after splitting off q H^+ ions and taking up p of the same, it is to be expected that the dissociation as represented in the above equation will in the main be a function of the pH of the solution in which the particle is suspended. Under the working conditions used the main process has been one of splitting off hydrogen ions, owing to the fact that the pH is considerably on the basic side of the isoelectric point. Because of this splitting off of hydrogen ions, the particle will be negatively charged. Consequently, the cations in the solution will tend to form an ionic atmosphere around it. In our particular case, these cations will be sodium ions. In the ionic atmosphere, the number of cations in excess of anions will be exactly enough to bring about electro-neutrality of the particle and the surrounding solution. A further assumption which we permit ourselves to make is that no metallic cations can occupy positions analogous to hydrogen in the OH groups, i.e., form covalent complexes of the type $O \cdot Na$ with either alumina or silica.

With the above assumptions in mind, the cation-exchange capacity of the aluminum silicate for Na^+ or other cation may be taken as a measure of the algebraic sum of the charges on the particle. In this algebraic sum, the charge of all ions, contained in the particle in the form of sterically hindered ions, will be included. And any positive charges on the surface of the particle, which may have resulted from taking up hydrogen ions, are to be made a part of the summation.

With this as a picture it is obvious that the cation-exchange capacity must vary inversely to exactly the same extent as the particles take up or give off hydrogen ions. By adding acid or base to the suspension containing salts of known concentration and making electrometric titration curves, one obtains a measure of the hydrogen ions taken up or given off as a function of the pH. In order to calculate this function it is only necessary to make a similar titration using a salt solution of the same composition as that in which the precipitate is suspended. The difference between the amount of acid or base, as the case may be, used to bring the suspension in a salt solution to a certain pH and that required to bring the salt solution alone to the same pH, gives the value of the hydrogen ions taken up or given off respectively by the precipitate. Thus from the two titration curves it is possible to calculate the change in cation-exchange capacity with pH.

It is to be expected from thermodynamic considerations and is shown to be the case for zeolites by Rothmund (4) and Kornfeld, and for soil silicates by Riehms (3) that for constant composition of the cation-exchanging substance the dependence of the pH on the concentration of the salt in suspension will be logarithmic. If we decrease the pH by one unit the concentration must increase by tenfold for a univalent ion, by a hundred-

fold for a divalent ion, by a thousandfold for a trivalent ion, etc. From this and the titration curves for the various cations, we may compute the functional relations between the cation-exchange capacity, the pH, and the cation concentration.

EXPERIMENTAL

*Preparation of the "aluminum silicate"*²

A specially prepared silica was used in preparation of the aluminum silicate. A typical example of the method used will be given. A Kahlbaum preparation (250 g.) of silicon tetrachloride was hydrolyzed by dropping it from a separatory funnel into water (2 liters), keeping the mixture at a low temperature by surrounding the reaction vessel with cold water. Ten repeated washings and filterings with hot distilled water, at intervals of twelve or more hours, were found to give a sample of silica which was free from chloride ion and which upon treatment with hydrofluoric acid left a residue less than one hundredth of 1 per cent.

The aluminum silicate was prepared by dissolving the silica so obtained in a 3.8 *N* solution of sodium hydroxide, so that the molar concentration of silica was 1.9. This mixture was added to a boiling solution of aluminum nitrate (0.1111 *N*) containing methyl red, until a permanent yellow had just been obtained. About 60 cc. of the sodium silicate mixture was necessary for every 500 cc. of aluminum nitrate solution. The precipitate was boiled with continual stirring for half an hour. After cooling, the mixture was diluted ten or more times, and a series of decantings performed until no appreciable residue was found in the supernatant liquid, i.e., less than 2 mg. per 100 cc. The suspension thus formed was diluted so that the residue on evaporation and drying at 150°C. was nearly 0.01 g. per gram of suspension. In this form it was used for experimentation.

Method of treatment with silver nitrate

The method of experimentation was as follows: A known volume of suspension was centrifuged. The resulting gelatinous mass, from which supernatant liquid can be poured without loss of the disperse phase, was added to a known weight of silver nitrate solution and in many cases of sodium nitrate solution. The mixture was rotated slowly (about one revolution per minute) for a varying period up to twenty hours, which is necessary if complete equilibrium is desired. However, it was found that for many purposes one or two hours was sufficient. This suspension was again centrifuged, and the weight and silver content of the decant determined. These processes were repeated a varying number of times, accord-

² It is to be noted that the product obtained here is not aluminum silicate, but rather a complex of alumina and silica possessing OH groups at various points. For the sake of simplicity, this complex will be referred to as aluminum silicate.

ing to the specific purpose of the experiment. After decanting for the last time, the gel was analyzed for silver and a check made of the total silver found as compared with that used. In all cases except the one noted below, the Volhard volumetric method was used in the analysis for silver.

Calculation of amount of silver taken up by the aluminum silicate

The following formula is used in the calculation of the silver taken up by the precipitate,

$$Ag_s = \frac{C_{Ag} G_{Ag} C (G_{Ag} + G_{Na} + G_{H_2O})}{\alpha [1 - C/1000 \times (M_{Ag} - M_{Na})]}$$

where

- Ag_s = millimoles of silver taken up per gram of original precipitate dried at 150°C.,
- C_{Ag} = concentration of silver nitrate solution (moles per 1000 g. of solution) added,
- G_{Ag} = grams of silver nitrate solution added,
- C = concentration of silver nitrate in solution decanted (moles per 1000 g. of solution),
- G_{Na} = grams of sodium nitrate solution added,
- G_{H_2O} = grams of water in the gel (or sometimes the suspension, if used instead),
- α = grams of precipitate used (dry weight at 150°C.),
- M_{Ag} = atomic weight of silver, and
- M_{Na} = atomic weight of sodium.

Time required to reach equilibrium

Table 1 shows the effect of time of treatment upon the amount of silver taken up by the precipitate. There were roughly 100 cc. in the final suspension and a dry weight of precipitate of about 1 g. In the second column is found the number of millimoles of silver (Ag_s) taken up by 1 g. of precipitate (dry weight at 150°C.). In the third and fourth columns are found the respective concentrations of silver and sodium in the decanted solution, expressed in moles per 1000 g. of solution. The parentheses around the numbers in the column giving the sodium concentrations indicate that these numbers are obtained by indirect calculation. All numbers without such parentheses have been obtained by direct experimental measurements. The last column gives the value of the check, ρ , of the experimental accuracy in the determination for silver. This is defined by

$$\rho = \frac{\text{Number of moles of silver found} - \text{number of moles of silver used}}{\text{Number of moles of silver used}}$$

It was found that four of the above-mentioned treatments of the gel from 100 cc. of suspension with 100 cc. of 1 *N* silver nitrate were sufficient to saturate the precipitate with silver. The maximum amount of silver which can be introduced into the precipitate by repeated treatments with solutions of silver nitrate is called the cation-exchange capacity with respect to silver, and is given in millimoles of silver per gram of "sodium" precipitate dried at 150°C.

TABLE 1
Time required to reach equilibrium

TIME OF TREATMENT WITH SILVER NITRATE	Ag _s	Ag _l	Na _l	$\rho \times 10^3$
5 min.	1 63	0 0833	(0.0084)	-2
1 hr.	1 72	0 0843	(0 0088)	-3 2
20 hrs.	1 80	0 0824	(0 0084)	-2
45 hrs.	1.79			

Ag_s = silver taken up by the aluminum silicate (millimoles per gram). Ag_l, Na_l = concentrations of silver and sodium respectively in the solution. ρ = check of experimental accuracy.

TABLE 2
Comparison of silver taken up with sodium given off

SAMPLE	NaNO ₃ 1ST DECANT	NaNO ₃ 2ND DECANT	NaNO ₃ 3RD DECANT	NaNO ₃ 4TH DECANT	NaNO ₃ 5TH DECANT	NaNO ₃ 6TH DECANT	NaNO ₃ TOTAL	Ag FOUND	$\rho \times 10^3$
1	1 54	0 17	0 06	0 01	0 00	0 00	(1 78)	1 76	-1 5
2	1 55	0.17	0 06	0 01	0 00	0 00	(1 79)	1.76	-1.7

Demonstration that the process is an exchange of silver with sodium

Table 2 gives the sodium nitrate found in the successive decants of an experiment consisting of six treatments of a gel from 100 cc. of suspension with 100 cc. of 1 *N* silver nitrate solution. The silver was precipitated from the decants as silver chloride and the sodium nitrate in the filtrates estimated by evaporation and conversion to sodium chloride upon repeated evaporation with concentrated hydrochloric acid. The total sodium is then compared with the amount of silver which has entered the precipitate, as determined by the titration of the final gel for silver. The value for silver in the precipitate, 1.76 millimoles per gram, agrees favorably with the values, 1.78 and 1.79 millimoles per gram of precipitate, obtained for sodium in the decants, and shows that the process is a true exchange of silver for sodium. We may conclude from this that the amount of nitrate ion entering the precipitate during an experiment is negligibly small.

From the method of preparation of the suspension, i.e., removal of all foreign salts by repeated decanting, it is to be expected that the nitrate-ion content in the precipitate should be negligibly small. A colorimetric test showed that the amount of nitrate ion was of the order of 0.005 millimole per gram. Since the nitrate ion does not form complexes either with silica or alumina, and since there is a large *negative* charge on the particle, it is probable that this small amount of nitrate ion has been retained in the interior of the precipitated particles and is thereby prevented from escaping because of steric hindrance.

Part of the sodium sterically hindered

The question arises here as to whether all the sodium contained in the precipitate can be exchanged or not. In this connection a determination of the cation-exchange capacity gave 1.79 millimoles per gram, while an analysis made at the same time on the same sample gave 2.01 millimoles per gram. It then appears that there is a small amount of sodium, i.e., $2.01 - 1.79$ or 0.22 millimole per gram not exchangeable for silver. It may be noted that this non-exchangeable sodium in the precipitate must be considered as forming such a part of the interior structure as to be thereby prevented from exchanging because of steric hindrance.

Cation-exchange capacity as a function of the age of the aluminum silicate

We will now discuss the cation-exchange capacity as a function of the age of the aluminum silicate. Experiments on the freshly prepared suspension of table 2 gave the value 2.11 millimoles per gram, while the experiments of table 2, which were performed from three to four months later, gave 1.76 millimols per gram. This change was checked by an analysis of the supernatant liquid from the suspension after standing for this period. This gave for sodium in the liquid phase 0.38 millimole per gram of precipitate in the suspension, which agrees well with the difference $2.11 - 1.76 = 0.35$. At this point it is of interest to note that the dry residue (red heat) found in the supernatant liquid was 5.9 per cent of the dry weight ($150^{\circ}\text{C}.$) of the total precipitate. The relative amounts of the various constituents are given in table 3. It will be seen that the relative amounts of Al_2O_3 and SiO_2 are rather closely the same in the two cases, but that there is considerably more Na_2O in the residue from the supernatant liquid than in the precipitate itself. The ratio by weight of silica to alumina in the case of the precipitate is 2.8 to 1, while in the case of the residue from the supernatant liquid it is 3.1 to 1. It is of interest to compare this fact of a nearly unchanged ratio of silica to alumina with the theory of Mattson, who maintains that the weathering always proceeds in such a way that the isoelectric point is approached. From Mattson's work one would

expect a considerably larger ratio of silica in the supernatant liquid than in the precipitate itself. According to Mattson's principle of the isoelectric weathering, a precipitate is most stable at the pH corresponding to the isoelectric point. The isoelectric point of our suspension is a little greater than 4, as shown by figure 2. However, on bringing the suspension to the isoelectric point by adding the calculated amount of nitric acid, it was found that about 10 per cent of the alumina and about 1 per cent of the silica were dissolved. This fact indicates that the isoelectric point is not the pH at which the suspension is most stable. This leads one to the conclusion that the factors governing the stability of the alumina-silica complex are not mainly electrostatic, but also depend considerably on the chemical constitution of the system.

TABLE 3
Relative amounts of the various constituents

CONSTITUENT	PRECIPITATE	DRY RESIDUE FROM THE SUPERNATANT LIQUID
	<i>per cent</i>	<i>per cent</i>
SiO ₂ .	60 33	60 2
Al ₂ O ₃ .	21 64	19 6
Na ₂ O . . .	4 11	20 2
H ₂ O	13 92	

Measurement of the equilibrium relations for silver-sodium

Having considered the question of the cation-exchange *capacity* of the aluminum silicate with respect to the exchange of silver and sodium, a word now will be said with regard to the equilibrium states in which only part of the exchangeable sodium has been exchanged for silver. Table 4 gives a summary of some experimental results. The quantities present are the same as those of table 1. In figure 1 the logarithm of the ratio of the concentrations of sodium to silver in the liquid phase, $\log \left[\frac{(\text{Na})}{(\text{Ag})} \right]$, is plotted against the logarithm of the ratio sodium to silver taken up by the precipitate, $\log \left[\frac{(\text{Na})}{(\text{Ag})} \right]$, as calculated from the values of the saturation capacity obtained experimentally. Two straight lines are found, one for the freshly prepared suspension, another for the suspension from twelve to sixteen weeks old. Several points of intermediate age are also found. It will be noted that, in the case of the suspension from twelve to sixteen weeks old, the points are much more diffusely scattered than is the case for the freshly prepared precipitate.

TABLE 4
Measurement of equilibrium relations for silver-sodium

EXPERIMENT	SAMPLE	Ag _s	Ag _l	Na _l	$\rho \times 10^3$	TIME OF ROTATION
						hours
1	2	1.80	0.0824	(0.0093)*	-2	20
2	1	1.81	0.0816	(0.0071)	-1.1	20
2	2	1.52	0.0380	(0.0384)	-0.8	20
2	3	1.58	0.0317	(0.0170)	-0.8	20
3	1	1.97	0.0762	(0.0165)	-1.5	20
3	2	1.80	0.0388	(0.0688)	-2.7	20
3	3	1.18	0.0404	(0.511)	-3.7	20
3	4	1.12	0.0409	(0.510)	-2.9	20
3	5	0.29	0.0508	(5.10)	-5.4	20
3	6	0.30	0.0509	(5.00)	-6.7	20
4	1	1.83	0.02281	(0.0237)		15
4	1	2.12	0.1472	(0.0313)	-1.4	20
4	2	1.87	0.02447	(0.0239)		15
4	2	2.10	0.1498	(0.0298)	-0.1	20
6	1	(1.54)	0.910	0.0105		2
6	1	(1.71)	0.990	0.0012		15
6	1	1.75	0.997	0.0004	-2.7	20
6	2	(1.54)	0.909	0.0105		2
6	2	(1.71)	0.990	0.0012		15
6	2	1.75	0.999	0.0004	-4.8	20
6	3	(1.54)	0.908	0.0104		2
6	3	(1.71)	0.991	0.0013		15
6	3	1.77	1.000	0.0005	-3.5	20
7	1	(1.54)	0.911	0.0104		2
7	1	(1.71)	0.991	0.0012		15
7	1	(1.77)	0.998	0.0004		20
7	1	(1.78)	0.999	0.0001	-3.5	20
7	2	(1.55)	0.912	0.0105		2
7	2	(1.72)	0.990	0.0012		15
7	2	(1.78)	0.999	0.0004		20
7	2	(1.79)	1.000	0.0001	-4.5	20
8	1	0.19	0.1121	(3.589)	-1	
8	2	0.20	0.1117	(3.582)	-2	20
8	3	0.48	0.1452	(0.926)	-1	20
8	4	0.52	0.1446	(0.995)	-3	20
8	5	1.42	0.1528	(0.0104)	-0.5	20
8	6	1.44	0.1529	(0.0105)	-3	20
9	2	1.30	0.533	(0.432)		20
9	3	0.74	0.0866	(0.765)		20
9	5	0.14	0.0673	(0.873)		20
9	6	0.13	0.0673	(0.872)		20

Ag_s = millimoles of silver in the precipitate per gram of sodium precipitate used.
 Ag_l = concentration of silver in the liquid phase. Na_l = concentration of sodium in the liquid phase.

* All numbers in parenthesis are not directly measured.

Titration of the aluminum silicate

Several samples of the suspension were prepared. One contained only water³ as suspending agent. The others contained various added electrolytes, sodium nitrate, sodium chloride, potassium chloride, silver nitrate, calcium nitrate, barium nitrate, and lanthanum nitrate, each of a concentration of 0.1 *N*. The pH values of these samples were determined. The results of these determinations are shown in table 5. A number of titration curves with the addition of 0.1 *N* nitric acid and sodium hydroxide

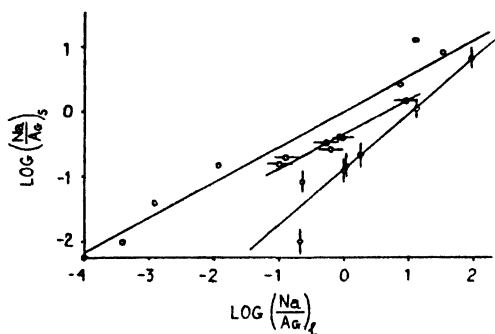


FIG. 1

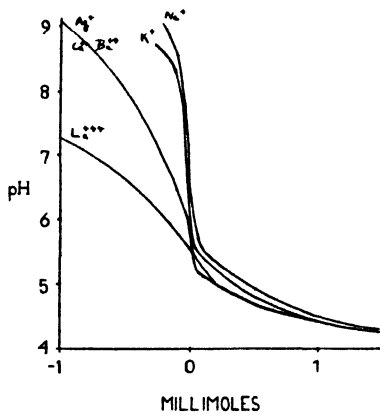


FIG. 2

FIG. 1. Equilibrium relations for the exchange of silver and sodium. The logarithm of the ratio of the concentration of sodium to silver in the liquid phase, $\log \left[\frac{\text{Na}}{\text{Ag}} \right]_l$, is plotted as abscissa against the logarithm of the ratio of the same elements in the solid phase, $\log \left[\frac{\text{Na}}{\text{Ag}} \right]_s$, as ordinate. \circ represents points for the freshly prepared suspension; \circ represents points for the suspension from twelve to sixteen weeks old; \circ represents points for the suspension of intermediate age.

FIG. 2. Titration curves for the aluminum silicate suspension containing various ions in one-tenth normal solutions. The pH is plotted against the amount of 0.1 *N* nitric acid or 0.1 *N* sodium hydroxide added expressed in millimoles per gram of precipitate dried at 150°C.

solutions were made on each of these samples of the suspension (see table 6). The titrations of the suspension containing silver nitrate were performed with the glass electrode. In that case neither hydrogen nor quinhydrone electrodes can be used, the hydrogen electrode because of the presence of the NO_3^- ion, and the quinhydrone electrode because of the reduction of silver nitrate to metallic silver. In all the other cases the quinhydrone

³ Sodium is present in the equilibrium concentration of about 0.004 *N*, after centrifuging and decanting the suspension from twelve to sixteen weeks old.

electrode was used. Comparison was made between the glass and the quinhydrone electrode for the case of the suspension containing sodium chloride, and a pH value of 6.36 was found for the quinhydrone electrode compared with 6.37 found for the glass electrode. Table 6 gives the pH as a function of the amount of acid added to each suspension. The first column gives the salt used, the second the amount of acid added in millimoles per gram of precipitate (dried at 150° C.), and the last the corresponding pH. In all cases 0.840 g. of precipitate, 0.0843 *N* nitric acid, and an original volume of 100 cc. were used.

It was found that the reproducibility of the experiments was poor on the basic side of the pH range. As an example of the dependence of minor

TABLE 5
*Values of pH in untitrated suspensions**

SUSPENSION CONTAINED IN	pH
Water.	7 7 (hydrogen electrode) 7 68 (quinhydrone electrode) 7 73 (glass electrode) 7 69† (quinhydrone electrode) 7 71† (glass electrode)
NaNO ₃ (0.1 <i>N</i>)	6 39
NaCl (0.1 <i>N</i>)	6 36
KCl (0.1 <i>N</i>)	6 35
AgNO ₃ (0.1 <i>N</i>)	5 98
Ca(NO ₃) ₂ (0.1 <i>N</i>)	5 99
Ba(NO ₃) ₂ (0.1 <i>N</i>)	6.00
La(NO ₃) ₃ (0.1 <i>N</i>)	5 58

* All numbers not specifically noted were obtained by use of the quinhydrone electrode.

† These values were obtained after the suspension had been "purified" by centrifuging, adding water to same volume as before, and allowing to stand one hour.

factors on the resulting pH in this region, the following example is cited. Using a sample of suspension containing 0.1 *N* sodium chloride, if 2 cc. of 0.1115 *N* sodium hydroxide is added all at once the resulting pH is 8.58, but if it is added in amounts of 0.5 cc. at intervals of ten minutes, the value obtained is 8.74.

Figure 2 shows the results which are considered to be best for the different ions in the 0.1 *N* solution. The pH is plotted against the amount of nitric acid and of sodium hydroxide added (both in millimoles per gram of precipitate). Examining these curves it will be noted that the lower the pH the less the specific effect due to each ion. This is to be expected, since the more acid the suspension the lower the net electrical charge and hence the specific effects, which are assumed to be in part electrostatic, will be

TABLE 6

Titration of the suspension with nitric acid (0.0843 N) using quinhydrone electrode

In all cases, weight of precipitate = 0.840 g. and original volume = 100 cc.

SALT	ACID ADDED IN MILLI- MOLES PER GRAM	pH*	MEAN	SALT	ACID ADDED IN MILLI- MOLES PER GRAM	pH*	MEAN
No salt	0 00	7 70†		NaCl (0.1 N)— <i>Concluded</i>	1 51	4 32	4.30
	0 10	6 96				4 30	
	0 20	6 48				4 30	
	0 50	5 66				4 29	
	1 00	3 85		KCl (0 1 N)	0 00	6 34	6 35
	1 51	3 32				6 38	
NaNO ₃ (0 1N)	0 00	6 69				6 35	
	0 10	6 02				6 34	
	0 20	5 73			0 10	5 77	
	0 50	5 08				5 78	
	1 00	4.49				5 80	
	1 51	4 23				5 76	
NaCl (0 1 N)	0 00	6.38	6 37	0 20	5 42	5 40	
		6 36			5 41		
		6 36			5 39		
		6 39			5 39		
	0 10	5 89	5 89	0 50	4 83	4 83	
		5 89			4 84		
		5 89			4 84		
		5 86			4 80		
	0 20	5 53	5 50	1 00	4 42	4 43	
		5 51			4.42		
		5 48			4 44		
		5 47			4 46		
	0 50	4 96	4 94	1 51	4 25	4 26	
		4 98			4 26		
		4 93			4 25		
		4 90			4 27		
	1 00	4.57	4 57	AgNO ₃ (0.1 N)	0 00	5 98	
		4 57			0 10	5 43	
		4 52			0 20	5 14	
		4 60					

* Each number shows an individual experiment. Thus in many cases it can be seen how much the values varied upon repetition.

† This value is the mean of the values obtained from the glass and quinhydrone electrodes.

TABLE 6—*Concluded*

SALT	ACID ADDED IN MILLI- MOLES PER GRAM	pH*	MEAN	SALT	ACID ADDED IN MILLI- MOLES PER GRAM	pH*	MEAN
AgNO ₃ (0.1 N)— <i>Concluded</i>	0.50	4.69		Ba(NO ₃) ₂ (0.1 N) — <i>Concluded</i>	0.20	5.12	
	1.00	4.41			0.50	5.67	
	1.51	4.24			1.00	4.38	
Ca(NO ₃) ₂ (0.1 N)					1.51	4.21	
	0.00	5.99		La(NO ₃) ₃ (0.1 N)	0.00	5.58	
	0.10	5.39			0.10	5.27	
	0.20	5.10			0.20	5.05	
	0.50	4.67			0.50	4.69	
	1.00	4.24			1.00	4.38	
Ba(NO ₃) ₂ (0.1 N)	0.00	5.99			1.51	4.21	
	0.10	5.42					

reduced. It will also be noted that nearly the same curve is found for the sodium and potassium ions and likewise one for silver, calcium, and barium ions. It is not understood why silver ion follows the curve for the divalent ions calcium and barium, but it must be supposed that there are specific effects which lead to this result.

From the curves of figure 2 we may calculate, on the basis of the considerations and postulates made in the theoretical section, the relations between the cation-exchange capacity and the pH. From the experimental results the value of the amount of exchangeable sodium ions in the untitrated suspension, to which neither acid nor base have been added, is 1.78 millimoles per gram. This value was found by treating the suspension with silver nitrate. Figure 3 shows the results of these calculations. The cation-exchange capacity, S , is plotted against the pH for 0.1 N solutions of the various cations in the suspension.

To check this relation between the pH and the cation-exchange capacity, calculated from the titration experiments, the amount of sodium ions exchangeable with silver ions has been measured at pH 5.10 in 0.1 N sodium chloride, and found to be 1.38 millimoles per gram. According to the curve in figure 3, we see that at pH 5.10 the value 1.37 is found and, conversely, at the cation-exchange capacity of 1.38 millimoles per gram the pH 5.08 is given. This agreement is very close and perhaps is better than should be expected.

Reversibility of titration

The question of the reversibility of these titrations is of interest. In order to determine this, the suspensions containing 0.1 N sodium and

potassium chlorides respectively were titrated back after first having been titrated forward with acid and base, respectively. Figure 4 shows the

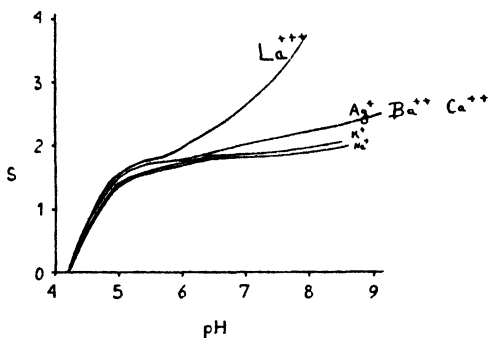


FIG. 3

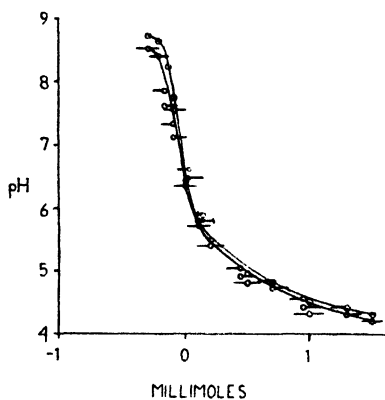


FIG. 4

FIG. 3. Relation between the cation-exchange capacity, S , and pH for one-tenth normal solutions of the various cations in the suspension.

FIG. 4. Titration of the aluminum silicate suspension in tenth normal solutions of potassium chloride and sodium chloride, showing back titration points. \circ represents the forward titration for sodium; $-\circ$ represents the forward titration points for potassium; $\circ-$ represents the back titration points for sodium; $\circ-$ represents the back titration points for potassium. In one case, where there may be ambiguity, the back titration points for Na^+ and K^+ , after the addition of base, are shown by $\circ-$ and $\circ-$, respectively.

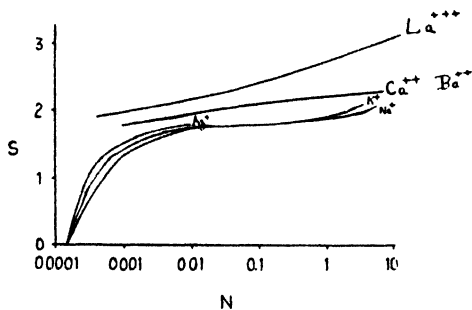


FIG. 5

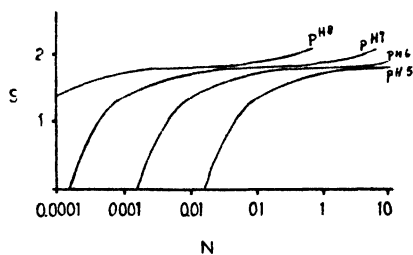


FIG. 6

FIG. 5. The relation between the cation-exchange capacity, S , and the salt concentration, N , at pH = 7

FIG. 6. The relation between the cation-exchange capacity, S , and the salt concentration, N , in the case of sodium ion at several pH values.

results of these experiments. It will be noted that there is a certain degree of irreversibility in the curves on the basic side of the pH range, but that

the irreversibility is negligible on the acid side. From this fact and the difficulty in obtaining reproducibility on the basic side, we may conclude that the precipitate is unstable in such solutions. Considering further the results of the breaking down of the precipitate and its solubility in acid solutions near the isoelectric point, it seems that the pH of maximum stability must lie at neutrality or at a somewhat lower pH. Comparable results have been obtained by Richms on clays.

It has been thought of interest to calculate the relation between the cation-exchange capacity, S , and the cation concentration, N , for a given pH, say 7 (see theoretical part). The results of these calculations are shown in figure 5. The cation-exchange capacity is plotted against the logarithm of the cation concentration. The values of the logarithms are not expressly given in figure 5, which shows only the values of the concentrations from which the logarithms were calculated. Figure 6 gives the same relation for sodium ion at several pH values.

SUMMARY

The theoretical aspects of the colloidal aluminum silicate particle are discussed. It is shown that the cation-exchange capacity will depend upon the pH of the suspending solution and upon the nature and concentration of salts present in the solution.

Experimentally, a single type of aluminum silicate was prepared. The conditions of preparation of this aluminum silicate are given in detail. The method of experimentation for the direct measurement of silver taken up by the aluminum silicate is explained. It is demonstrated that the process is a mole-for-mole exchange of silver for sodium, and that a small part of the sodium is non-exchangeable by silver. It is pointed out that the cation-exchange capacity depends on the age of the sample. The equilibrium relations where only part of the silver has been exchanged have been measured and discussed. pH determinations and titration curves were made on the suspension containing a number of salts in tenth normal solution. Calculations based on the theoretical picture were made and discussed.

The author wishes to express his sincerest appreciation to Prof. N. Bjerrum and to the American Scandinavian Foundation for making possible the carrying out of the above research.

REFERENCES

- (1) The most important literature references are noted here for the subject as a whole. Specific references are made at the appropriate points.
GEDROIZ, K. K.: *Soil Sci.* **16**, 473-4 (1923).
GEDROIZ, K. K.: *Kolloidchem. Beihefte* **33**, 317-448 (1931).
Goy, S.: *Ergebnisse Agrikultur Chem.* **2**, 35-52 (1930).

- KELLEY, W. P., AND BROWN, S. M.: Calif. Agr. Expt. Sta. Tech. Paper No. 15 (1924).
- KERR, W. H.: Soil Sci. **26**, 385-98 (1928).
- MAGISTAD, O. C., AND BREAZEALE, J. F.: Univ. Arizona Tech. Bull. No. 34 (1928).
- MATTSON, SANTE: Kolloidchem. Beihefte **14**, 227-316 (1922); Soil Sci. **23**, 179-220, 373-407 (1929); **31**, 311 (1931).
- MATTSON, SANTE: Soil Sci. **30**, 459 (1930); **31**, 57 (1931); J. Am. Soc. Agron. **18**, 458-70 (1926); J. Agr. Res. **33**, 553-67 (1926); Proc. First Internat. Cong. Soil Science **2** (Comm. II), 185-98, 199-211 (1927); Soil Sci. **25**, 289-311 (1928); J. Phys. Chem. **32**, 1532-52 (1928).
- TRUOG, E.: J. Am. Soc. Agron. **21**, 1030 (1929).
- WIEGNER, GEO.: Kolloid-Z. **36** (Ergänzungsband), 341-448 (1931).
- (2) The references for the more important theories as to the nature of the colloidal particle which are relevant to the concept of cation exchange are the following:
- McBAIN, J. W.: Nature **112**, 865 (1923).
- EVANS, U. R., AND BIRCUMSHAW, L. L.: Kolloid-Z. **34**, 65-72 (1924).
- McBAIN, J. W.: Kolloid-Z. **40**, 1-9 (1926).
- MALFITANO, G., AND SIGAUD, M.: J. chim. phys. **24**, 103-9 (1928).
- WINTAGEN, R., AND KUHN, O.: Z. physik. Chem. **138A**, 135-57 (1928).
- RANDALL, M., AND CANN, J. Y.: Chem. Rev. **7**, 369-406 (1930).
- (3) ROTHMUND, V.: The Royal Veterinary and Agricultural College Yearbook, pp. 60-8. Copenhagen (1932).
- (4) ROTHMUND, V.: Z. Elektrochem. **32**, 361 (1926).
- KORNFELD, G.: Z. Elektrochem. **23**, 114 (1917).
- ROTHMUND, V., AND KORNFELD, G.: Z. anorg. Chem. **103**, 129 (1918).

CATHODE POLARIZATION AS A FUNCTION OF THE CURRENT DENSITY IN FUSED SALTS

S. KARPATSCHOFF AND O. POLTORATSKA

Institute of Physical Chemistry, Scientific Researches, Sverdlovsk, U. S. S. R.

Received December 5, 1935

Cathode polarization in fused salts has been studied very little up to the present time. There is one paper by Aten and others (1), but Aten was interested only in the relation between the cathode potential and the current density in connection with the character of cathode deposits obtained from fused salts. Our method of experimenting was the same in principle as that used by Aten. The fused salt in a porcelain crucible was placed in an electric furnace with the carbon electrodes—cathode and anode—passing through the opening in the cover of the furnace. The potential was measured between an auxiliary electrode and the cathode at various current densities. The auxiliary electrode was constructed in the following way. The fused metal being plated was placed at the bottom of a quartz test tube with capillary jet at the side which was closely pressed to the cathode. The test tube was filled with fused electrolyte through the capillary jet; thus a lead or cadmium electrode was obtained. The contact of liquid metal in the test tube with the wires connected to the potentiometer was made by means of an iron wire. This wire was enclosed in a porcelain capillary in order to prevent contact of the iron wire with the fused electrolyte. We measured the resistance of the cathode in order to make the necessary correction. In this measurement the cathode was at the same temperature condition as that during the investigation at cathode polarization. The highest possible error was 0.01–0.02 Ω in the determination of cathode resistance.

In the case of lead chloride the curve $E_{\text{cath}} = f$ (current density) has the form shown in figure 1. It is seen that the potential of the cathode is more positive than the potential of the auxiliary electrode at comparatively low current densities. The cathode potential becomes less and less positive by increasing the current density and finally equals the potential of the auxiliary electrode (figure 1, point A). The current density at point A is equal to 0.2–0.15 ampere per square centimeter. Thus electrolysis of fused lead chloride at significant current densities can take place when the difference of the potentials between the electrodes is less than the E.M.F. of the system $\text{Pb}(\text{PbCl}_2 \text{ fused}) \text{Cl}_2$. The effect indicated was previously noticed

by R. Lorenz (3), who explains the phenomenon as a depolarizing action. This is confirmed by the fact that we were able by saturating the fused lead chloride with metallic lead to reduce the current density, at which the curve $E_{\text{cath}} = f(\text{current density})$ crosses the axis of the ordinates, from 0.2 amp. to 0.015 amp. It is known that lead chloride can "dissolve" a significant quantity of metallic lead. R. Lorenz supposed that in this case an emulsion of the lead is formed in the fused salt. However, Eitel and Lange (2) showed that the metal is not in colloidal form, but in true solution. The solution of the metal in the fused salt is explained by these authors by the formation of compounds of metallic lead with lead chloride.

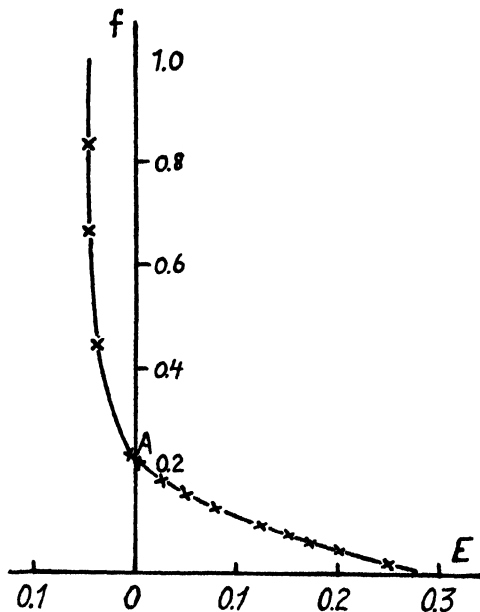


FIG. 1

The part of the curve that lies in the region of the positive values of potential can be explained by assuming that during the dissolution of metallic lead in the fused salt monovalent lead ions are formed. Consequently it is possible that in the case of absence of metal in fused salt during electrolysis the discharge of Pb^{++} ions to Pb^+ ions took place at the cathode. The potential of the cathode may be expressed in the following form:

$$E = a - \frac{RT}{F} \ln \frac{C_{\text{Pb}^+}}{C_{\text{Pb}^{++}}} \quad (1)$$

where a is constant, and C_{Pb^+} and $C_{\text{Pb}^{++}}$ are the concentrations of the mono- and bi-valent ions near the cathode.

Reasoning by analogy from the case of concentration polarization in water solutions, C_{Pb^+} and $C_{\text{Pb}^{++}}$, and placing their values in equation 1 we have

$$E = a - \frac{RT}{F} \ln \frac{K_1 D - C_0}{C_0^1 - K_2 D}$$

Here K_1 and K_2 are constants at a given temperature; C_0 and C_0^1 are the concentrations of the ions Pb^+ and Pb^{++} in the mass of the electrolyte. C_0 is insignificant (the fused salt was not in contact with the metal). Dividing the numerator and the denominator of the logarithmic fraction by C_0^1 and combining all constants in a , we shall finally have:

$$E = a - \frac{RT}{F} \ln \frac{D}{1 - KD} \quad (2)$$

The value of the constant a is determined by the condition that the difference of the potentials between cathode and auxiliary electrode is zero at a certain current density, D_0 (point A, figure 1).

$$a = \frac{RT}{F} \ln \frac{D_0}{1 - KD_0}$$

Putting the value of a in equation 2 we shall have:

$$E = \frac{RT}{F} \ln \frac{D_0 (1 - KD)}{(1 - KD_0) D} \quad (3)$$

The results of the experiments with fused lead chloride at 600°C. and the values of the constant K are shown in table 1.

The part of the curve $E = f$ (current density) was studied for fused lead chloride in the region of the negative values of potential in experiments 2, 4, and 5 at 550°C. The results of these experiments are shown in table 2.

In a given case the relation $E = f$ (current density) may follow an equation of the form $E = a - b \ln D$. The coefficient b has the following values:

exp.	2	4	5
b.	0.0348	0.0391	0.0417

From the figures given it is seen that the coefficient b is approximately equal to the quantity $RT/2F$, which has the value 0.0354 at 550°C.

The relation obtained can be explained by supposing that in the region of the negative values of the potential the process $\text{Pb}^{++} + 2\ominus \rightarrow \text{Pb}$ on the cathode plays the coördinal rôle. In this case we can suppose that atoms of the metal which are formed at the cathode remain near it in the dissolved state and then these atoms condense in droplets with a certain definite

speed (the fused metal did not wet the carbon cathode). In connection with the above view, we can write the following expression for the potential of the cathode:

$$E = a - \frac{RT}{2F} \ln \frac{C_{Pb}}{C_{Pb^{++}}}$$

TABLE 1

Results of experiments with fused lead chloride at 600°C.

<i>E</i>	EXPERIMENT 1		EXPERIMENT 2		EXPERIMENT 3		EXPERIMENT 4	
	<i>D</i>	<i>K</i>	<i>D</i>	<i>K</i>	<i>D</i>	<i>K</i>	<i>D</i>	<i>K</i>
<i>volts</i>	<i>amp./sq. cm.</i>		<i>amp./sq. cm.</i>		<i>amp./sq. cm.</i>		<i>amp./sq. cm.</i>	
0.000	0.150		0.153		0.170		0.200	
0.025	0.130	4.00	0.130	3.50	0.150	3.84	0.180	3.54
0.050	0.107	3.74	0.110	3.95	0.137	4.32	0.157	3.44
0.075	0.090	3.96	0.093	3.97	0.120	4.40	0.140	2.92
0.100	0.073	3.76	0.087	4.00	0.107	4.74	0.117	3.64
0.125	0.063	4.40	0.067	4.40	0.097	4.78	0.100	3.73
0.150	0.050	4.40	0.060	4.80	0.083	4.21	0.087	3.90
0.175	0.040	4.50	0.050	5.05	0.067	3.40	0.073	3.99
0.200	0.033	4.70	0.040	5.02	0.043	4.84	0.057	3.97
0.250	0.020	4.90	0.023	5.05	0.023	4.34	0.030	3.69

TABLE 2

Results of experiments with fused lead chloride at 550°C.

EXPERIMENT 2		EXPERIMENT 4		EXPERIMENT 5	
<i>E</i>	<i>D</i>	<i>E</i>	<i>D</i>	<i>E</i>	<i>D</i>
<i>volts</i>	<i>amp./sq. cm.</i>	<i>volts</i>	<i>amp./sq. cm.</i>	<i>volts</i>	<i>amp./sq. cm.</i>
0.009	0.160	0.001	0.225	0.015	0.614
0.011	0.186	0.014	0.279	0.029	0.837
0.017	0.213	0.029	0.446	0.033	1.000
0.027	0.264	0.048	0.670	0.035	1.115
0.033	0.422	0.052	0.837	0.044	1.228
0.044	0.527			0.048	1.396
0.052	0.580			0.052	1.507
0.060	0.738				

C_{Pb} is the concentration of the atoms of lead which are in the dissolved state near the cathode. Regarding the value $C_{Pb^{++}}$ as constant, we shall have:

$$E = a - \frac{RT}{2F} \ln C_{Pb} \quad (4)$$

Assuming at each current density an equality between the speed of discharge of the ions Pb^{++} and the speed of condensation of the dissolved metallic atoms, we shall have:

$$KD = C_{\text{Pb}} - C_0 \quad (5)$$

where C_0 is the value of a concentration corresponding to equilibrium at a given temperature. Placing the magnitude C_{Pb} in the expression of potential and making some simplification, we shall finally have:

$$E = a - \frac{RT}{2F} \ln (1 + K_1 D) \quad (6)$$

If the constant K_1 is great enough, equation 6 may be written thus:

$$E = a - \frac{RT}{2F} \ln D \quad (7)$$

The curve $E = f$ (current density) in fused cadmium chloride is similar to the corresponding curves for lead chloride, only here the curve intersects

TABLE 3
Results of experiments with cadmium chloride

EXPERIMENT 6		EXPERIMENT 7			
<i>E</i>	<i>D</i>	<i>E</i>	<i>D</i>	<i>E</i>	<i>D</i>
<i>volts</i>	<i>amp./sq. cm.</i>	<i>volts</i>	<i>amp./sq. cm.</i>	<i>volts</i>	<i>amp./sq. cm.</i>
+0.120	0.006	-0.016	0.002	-0.084	0.044
+0.113	0.024	-0.022	0.006	-0.104	0.048
+0.081	0.045	-0.033	0.010	-0.117	0.066
+0.060	0.084	-0.048	0.014	-0.132	0.088
+0.033	0.253	-0.053	0.018	-0.141	0.110
+0.026	0.353	-0.067	0.026	-0.150	0.132
+0.004	0.446	-0.073	0.034	-0.157	0.176
-0.027	0.670				

the axis of the ordinates at greater current density (experiment 6). Saturating the fused cadmium chloride with metallic cadmium (experiment 7) we succeeded in reducing the value of this current density almost to zero; thus the total curve lies in the region of negative values of the potential.

The results of experiments 6 and 7 can be seen in table 3. In cadmium chloride the dependence $E = f(D)$ also seems to follow an equation of the form $E = a - b \ln D$. The coefficient b is equal to 0.0435 (experiment 6) and to 0.0348 (experiment 7), i.e., to $RT/2F$. In the region of the negative values of the cathode potential (experiment 7) the existence of the indicated relation can be explained in a similar way to that of chloride. The relation

$$E = a - \frac{RT}{2F} \ln D$$

for cadmium chloride, which is not saturated with metallic cadmium (experiment 6), can be explained by supposing that by dissolving the

metallic cadmium in its chloride salt the formation of the ions Cd^+ does not take place; thus on the cathode the process $\text{Cd}^{++} + 2\ominus \rightarrow \text{Cd}$ takes place. In connection with this, at all current densities the velocity of formation of the cadmium atoms will equal the velocity of their diffusion in the mass of the electrolyte. Thus we can write:

$$KD = C_{\text{Cd}} - C_0$$

where C_0 is the concentration of the cadmium atoms in the mass of the electrolyte. Determining the concentration of the cadmium atoms near the cathode, C_{Cd} , we obtain

$$C_{\text{Cd}} = KD + C_0$$

If C_0 is very small (the fused salt was not in contact with the metal), we shall finally have:

$$E = a - \frac{RT}{2F} \ln D$$

RÉSUMÉ

The cathode polarization in fused salts of lead chloride and cadmium chloride has been experimentally studied. The part of the curve $E = f(D)$, lying in the region of the positive values of the potential, is explained by the slowness of the diffusion process of Pb^+ ions or cadmium atoms from the cathode in the mass of the electrolyte.

In the region of the negative values of the potential the relation $E = f(D)$ can be expressed by the equation

$$E = a - \frac{RT}{2F} \ln D$$

We have explained the equation of this form by the slowness of condensation of the lead or cadmium atoms which are formed at the cathode in the liquid.

In conclusion we desire to express our thanks to Prof. A. N. Frumkin for his attention to this work.

REFERENCES

- (1) ATEN AND OTHERS: *Trans. Am. Electrochem. Soc.* **47**, 265 (1925).
- (2) EITEL AND LANGE: *Z. anorg. allgem. Chem.* **171**, 158 (1928).
- (3) LORENZ, R.: *Die Elektrolyse geschmolzenen Salze* (1904).

OXIDATION PROCESSES AT THE CATHODE

O. K. KUDRA AND K. N. IVANOV

*The Research Institute of Chemistry of the Ukrainian Academy of Sciences,
Kiev, U. S. S. R.*

Received April 30, 1936

The nature of the cathodal deposits in the electrolytic deposition of metals depends upon the conditions of the electrolysis. The same metal may deposit itself either in a solid smooth layer or in the form of crystals which grow into dendrites. At times the electrolysis is accompanied by the formation of a spongy mass on the cathode; sometimes the deposit takes the form of an entirely black porous powder.

With high current densities the deposition of metals takes place from dilute solutions in the form of porous, black, highly dispersed powders. Although this phenomenon has been known for a long time and a considerable amount of work has been done in this field, the problem is still not entirely cleared up.

The deposition of a black powder-like deposit on the cathode has been reported by many authors. As far back as in 1848 Poggendorf (12) reported the deposition of silver-black. Somewhat later Mylius and Fromm (8) described the formation of black deposits of platinum, zinc, cadmium, and lead. Later similar deposits were obtained for a number of other metals. We may now state definitely that under certain conditions black deposits can be obtained with almost all metals which form deposits on the cathode in electrolysis.

In a study of the cathodal processes in the electrolysis of copper salt solutions, one of the authors (6) found a definite relation between the concentration, the current density, and the time of the appearance of the black deposit. The observed regularity in the time when the deposit changes its appearance is undoubtedly connected with its structural and chemical composition. The authors have now studied in detail the structure and composition of the black deposits, using the röntgenographic method.

Black deposits of copper, zinc, cadmium, and silver, which settled out from dilute solutions of various salts at high current densities, were obtained. The reagents used were of "c.p. for analysis" grade. The experiments were carried out at room temperature. A 100-cc. beaker was used for a bath. The anode was a spiral of the metal and was placed at the

wall of the beaker, surrounding on all sides the cylindrical platinum cathode in the center of the beaker. This arrangement gave a uniform current density on the cathode ($= 1$ amp. per square centimeter). The porous black deposit of the metal (about 2 mm. thick), which settled out during the electrolysis, was quickly removed with the cathode to a beaker of hot distilled water and at once taken off from the electrode with a glass rod. The cathode was put back into the solution and the experiment was repeated until a sufficient quantity of deposit was collected. This was washed with hot water, dried between sheets of filter paper, and packed in a slightly damp state into straws for analysis by Debye's method.

The x-rays were obtained from Hadding's ionic tube with a copper anode and filtered through a nickel-filter; after filtration only the K_{α} rays with an average wave length of $\lambda_{\alpha} = 1.539$ A.U. remained. The röntgenogram data were calculated as the average values of four objective measurements. The error in the calculation of the parameters did not exceed 0.003–0.005 A.U.

It is characteristic of almost all the röntgenograms made that additional diffraction rings were present, and it was established that these were due to oxides. The relative intensities of the diffraction rings of the metals and their oxides were not always the same. The difference depends upon the chemical nature of the metal as well as upon the nature of the electrolyte from which the metal was deposited.

In general, the presence of oxides in electrolytic deposits is a well established fact (1, 3, 5), but the causes of their appearance are not fully investigated. Applying the relative intensity of the diffraction rings of the metals and their oxides as a criterion, we have determined the approximate content of oxides in various deposits. *The copper deposits* were studied most extensively. They consisted of metallic copper and of cuprous oxide. In none of the röntgenograms was cupric oxide discovered. Both copper and cuprous oxide were in a high state of dispersion, since the rings of the röntgenograms were slightly diffuse. Copper deposits were obtained from solutions of the nitrate, sulfate, and chloride and also the baked deposit from the nitrate. The results are given in table 1.

Table 1 shows that the deposits contain a considerable quantity of cuprous oxide. Foerster and Seidel (3), who first observed cuprous oxide in deposits of copper, gave an explanation for its formation. When cupric sulfate is electrolyzed under certain conditions, the cupric ion at the cathode is reduced to cuprous ion and cuprous sulfate is formed; the latter is hydrolyzed and cuprous oxide formed. R. Luther (7) supports this scheme. The results of our investigations, however, do not harmonize with this point of view. The comparison of the cuprous oxide contents of various deposits leads us to believe that the cuprous oxide is formed as a result of oxidation, which is effected mainly by the anion. The higher the oxidizing

power of the anion, the greater the oxide content in the precipitate. Besides this factor, other oxidizing factors are also taking part, as is shown by the presence of cuprous oxide in the deposits resulting from the chloride solution. Evidently the cupric cation and the hydroxyl ions of the solvent are also capable of exerting an oxidizing effect. It is possible that a hydrolysis process is also taking place, according to Foerster's scheme, but it seems to play a secondary rôle.

It is very interesting to note that both copper and cuprous oxide in the precipitates have greatly increased parameters of the crystalline grating. These increases vary with a certain regularity, the lower the oxide content in the precipitate the greater being the increase in parameter. At the same time the percentage increase in the parameters of copper and cuprous oxide of the same precipitate is almost the same. The increase in parameter is evidently due to the penetration of hydrogen into the crystalline grating,

TABLE 1
Results of the röntgenographic investigations

KIND OF COPPER DEPOSIT	Cu ₂ O			Cu		
	Approximate per cent in precipitate	Parameter of the grating	Per cent increase of parameter	Approximate per cent in precipitate	Parameter of the grating	Per cent increase of parameter
	<i>per cent</i>	<i>A.U.</i>		<i>per cent</i>	<i>A.U.</i>	
Precipitate from the nitrate	40-45	4 279	0 45	55-60	3 627	0 47
Precipitate from the sulfate	25-30	4 290	0 70	70-75	3 636	0 72
Precipitate from the chloride	10-15	4 300	0 94	85-90	3 642	0 90
Baked deposit from the nitrate	40-45	4 266	0 14	55-60	3.621	0 30

Copper and cuprous oxide crystallize in the cubic system. The normal parameters are: for copper $a = 3.61$ A.U.; for cuprous oxide $a = 4.26$ A.U.

with the formation of so-called solid solutions of the second order,—hydrogen dissolved in copper and in cuprous oxide. Electrolysis at high current densities occurs in conditions which are exceptionally favorable for the formation of solid solutions of hydrogen. The deposits settle out in a highly dispersed state. Parallel with the settling out, a discharge of the hydrogen ions takes place at the cathode and every crystalline particle of precipitate contains hydrogen on its surface during the whole process of growth. The higher the concentration of hydrogen on the growing particle, the greater is the quantity of hydrogen which will imbed itself into the crystalline grating and the greater the increase in the parameter. Simultaneously with this, secondary oxidizing factors are active at the cathode, affecting the particles of the precipitate as well as the hydrogen on their surface. Evidently, the more active the oxidizing factors are, the less hydrogen will be dissolved in the precipitate and the more oxides will be present.

From this point of view it is clear that the greatest increase in the parameters of copper and cuprous oxide should be observed with the chloride solution, since in this case the oxidation processes are the weakest. The reverse should be found with the nitrate solution.

Thus, the secondary oxidation processes at the cathode, connected with the oxidizing activity of the ions, affords a satisfactory explanation of the changes in the size of the parameters of the gratings of copper and cuprous oxide observed in our investigations.

The fact that the increase in parameter is observed not only in copper but also in cuprous oxide is of significance, since it proves that the oxidation of the metal by the anion is taking place during the whole process of precipitation of the metal and not only after the current is cut off.

In order to bring out the effect of heat on the deposition, one of the copper precipitates obtained from the nitrate was baked. This changed the color from dark-brown to the ordinary red color of copper. The diffraction rings of copper and cuprous oxide on the röntgenograms became very sharp, which indicates a decrease in dispersion. The size of the parameters of the grating decreased, especially for cuprous oxide, the parameter of which almost reached the normal size. At the same time the loss of hydrogen by the copper precipitate was small, in spite of the fact that in baking the metal was brought to a red heat. Evidently the copper grating is holding on very firmly to the dissolved hydrogen.

The zinc deposits studied were obtained from nitrate and from chloride solutions.

The precipitate obtained by the electrolysis of the nitrate was almost completely oxidized, while the electrolysis of the chloride gave a metal with an insignificant admixture of zinc oxide. This fact is analogous to the regularity observed in the precipitates of copper and confirms the oxidizing rôle of the anion. The solvent, evidently, plays a secondary rôle as an oxidizing factor.

The results with the zinc precipitates are an additional confirmation of the inapplicability of the hydrolytic view for the general explanation of the origin of the oxides present in the cathodal precipitates.

It is worthy of notice that while the precipitate from cupric nitrate contained 40–45 per cent of cuprous oxide, the precipitate from zinc nitrate contains almost completely oxidized zinc. This shows that the oxide content depends upon the degree of oxidizability of the metal.

Unlike copper, the deposited zinc has normal parameters of its crystalline grating. Evidently, zinc by its chemical nature is not capable of absorbing hydrogen. On the other hand, zinc oxide has a much enlarged parameter, more than 1.5 per cent, which shows a considerable quantity of dissolved hydrogen. *The cadmium deposit* was precipitated by electrolysis of the nitrate solution. Similar to the deposits from the nitrates of

copper and zinc, it contained only 40–50 per cent of metal. Unfortunately the röntgenogram was not definite as to the nature of the admixtures. Altogether we were able to measure seventeen diffraction rings, of which nine were those of cadmium; the other eight were rings of an unknown structure, definitely neither of cadmium oxide nor of cadmium hydroxide, the gratings of which are known. We assume that the admixture is Cd_2O , the structure of which is not known and which has been very little investigated. This assumption is strengthened by the fact that the deposit of copper, which is capable of forming two kinds of oxide, always contained only the lower oxide,—cuprous oxide. The metallic cadmium in the deposit has a considerably widened grating. The increase in the parameter is 1.08 per cent, which indicates a great absorption of hydrogen.

The silver deposit was also obtained from the nitrate solution. The deposit does not contain any oxide, the röntgenogram containing only the silver rings. The grating differed very little from the normal, and the

TABLE 2
Comparison of copper, zinc, cadmium, and silver

ORDER IN THE ELECTROMOTIVE SERIES	THEIR NORMAL POTENTIALS BY THE NORMAL HYDROGEN ELECTRODE	THE OXIDE CONTENT IN THE DEPOSIT FORMED FROM THE NITRATE
	volts	per cent
Zinc.	−0 76	97–98
Cadmium.	−0 40	50–55
Copper.	+0 34	40–45
Silver	+0 80	No oxide

increase hardly exceeds the possible experimental errors, hence silver dissolves hardly any hydrogen.

The deposits from the nitrates were obtained from all the metals under investigation—copper, zinc, cadmium, and silver. If we place the oxide content of the deposits in the order of the metals in the electromotive series, as in table 2, a definite regularity is seen. The oxide content diminishes with the diminished oxidizability of the metal. This confirms the idea expressed above.

Along with the oxidizing action there is also at the cathode a reducing action, due to the hydrogen set free. Its importance in the general process depends upon the deposition potential of the metal and upon the pH of the solution.

The sum of all the factors enumerated above determines the character of the secondary chemical process and the composition of the cathodal deposits in each particular case.

Thanks to the high dispersion state of the deposited metals, the changes

brought about by the secondary chemical processes become exceptionally augmented. The nature of the secondary processes, however, is not a function of the current densities, the same process but to a different degree taking place at both high and low current densities. Therefore all the conclusions reached for deposits formed at high current densities hold good also for electrolysis in ordinary conditions. Oxidation taking place during deposition causes heterogeneity of the deposit and has considerable influence on its physical structure.

SPONGY DEPOSITS

The above study led us to the idea that oxidation is also a possible cause of growth of the so-called spongy deposits on the cathode. The oxide content of deposits from nitrate solutions increases in the direction silver, copper, cadmium, zinc, i.e., it depends on the oxidation tendency of the metals. The tendency for spongy deposit formation, all other conditions being equal, follows the same order. The greater tendency of zinc for spongy deposit formation, as compared with cadmium, was reported as far back as 1897 by Mylius and Funk (10). Of the four metals mentioned, zinc has the greatest oxidation tendency and it is exactly in the electrolysis of this metal that spongy formations cause the greatest difficulties. In the earlier investigations, the zinc spongy formation was considered to be due to the action of hydrogen (4) and even the formation of a hypothetical hydride, ZnH_2 (14). Later, however, it was noted that the spongy mass is obtained in cases favorable for the formation of oxide. Mylius and Fromm (9) noticed the appearance of a spongy layer at the surface of a solution, where the air can exert its oxidizing effect, while inside a crystalline deposit is formed. It was also noted that the addition of hydrogen peroxide, oxygen-containing turpentine, or other oxidizing agents to the electrolyte favors sponge formation. Foerster and Günther (2) and Seborn (13) point out the influence of hydroxide ions on the formation of sponge, connecting this with formation of zinc hydroxide.

Although black pulverized metals are deposited at very high current densities and sponge formation occurs, mainly, at low densities, both phenomena are accompanied by the formation of oxides at the cathode. This was also well established with copper. Foerster and Seidel (3) and Kistiakovsky, Bymakov, and Krotov (5) show the presence of cuprous oxide in the deposits obtained at high as well as at very low densities. Some medium densities favor the deposition of pure metal.

Sponge formation was studied with zinc and cadmium. The electrodes consisted of the metal under investigation; the anode had the form of a rod, the cathode of a rectangular 3 cm. plate. The electrolyte was a solution of the sulfate. In the case of cadmium 0.01 per cent gelatin and 0.1 per cent H acid were added to the solution to avoid dendrite formation.

The zinc sulfate solution used was without additions. The experiments were carried out at room temperature.

The electrolysis of cadmium sulfate was carried out at current densities of 0.01 amp. per square centimeter. The electrolyte solution contained 10 per cent cadmium sulfate. The metal deposited at first in a compact smooth layer all over the surface of the cathode. Soon, however, a narrow strip of a gray spongy mass was clearly visible on the cathode at the very surface of the electrolyte solution. As time went on this mass spread downwards, gradually covering a larger and larger area of the cathode.

After an interval of about seven hours the sponge occupied about a quarter of the surface of the electrode. Towards the end of the experiment, which lasted about fifteen hours, the sponge covered considerably more than half the surface. The electrode was thoroughly washed and samples of the spongy and of the compact deposits were taken for the röntgenographical study. Experiments carried out under similar conditions, but with various additions to the electrolyte solution, showed that acidification of the solution always retards the appearance of spongy deposit. This deposition is also retarded by the addition of reducing substances. Thus the addition to the solution of even a relatively small amount of formaldehyde (0.2 per cent CH_2O) considerably retards the appearance, as well as the rate of growth of the spongy mass over the electrode. A reduction in the current density, similar to the one described in the literature (4, 11) for zinc, increases the tendency of spongy deposit formation for cadmium.

The electrolysis of zinc sulfate was carried out under similar conditions at a current density of 0.02 amp. per square centimeter. At this current density a sufficiently thick layer of solid zinc was obtained alongside with the spongy deposit.

The results of the x-ray study show that both spongy deposits—zinc and cadmium—contain oxides. The zinc deposit contains zinc oxide, and the cadmium, presumably Cd_2O . The additional rings on the last röntgenogram are identical with those which were found by us in the cadmium deposit obtained at high current densities. Although both spongy deposits contain oxides, the solid layers of zinc and cadmium consist of the pure metals.

The oxidation could be considered as due mainly to the anion of the salt, although other factors are not excluded. The fact that the sponge appears at first at the surface of the solution shows that oxidation is also effected by atmospheric oxygen. This contradicts the view that the appearance of oxides on the cathode is due to the hydrolysis of the salts. The conditions for hydrolysis are the same at the surface of the solution as within it. Neither does the hydrolytic interpretation of the presence of oxides explain the effect of hydrogen peroxide, oxygen-containing turpen-

time, and other oxidizing agents in favoring the sponge formation, nor does it explain the effect of reducing substances (CH_2O) in greatly retarding the process. It is also not clear why in the spongy deposits as well as in the black deposits obtained at high current densities only oxides are found, but not even traces of hydroxides, while the latter should undoubtedly be present if the process were accompanied by hydrolysis. All these isolated facts are completely explained by assuming that the process at the cathode consists of two opposite tendencies, reducing and oxidizing. The factors strengthening the latter tendency favor the formation of porous black and spongy deposits. The strengthening of the reducing tendencies, on the contrary, hinders this process. An increase in the concentration of hydrogen ions of the electrolyte, causing an increase in the amount of hydrogen liberated during electrolysis, should diminish the tendency to sponge formation. An increase in the current density has a similar effect. However, a great increase in the density augmenting the reducing processes causes at the same time a great increase in the state of dispersion of the deposited metal. Under certain conditions a point might be reached when the metal will deposit in a state of very high dispersion. This increases its oxidation capacities to such a degree that conditions favorable for oxide formation are again created and a porous structure again appears, which causes the formation of black powder-like deposits.

SUMMARY

An x-ray study of the powder-like cathodal deposits of copper, zinc, cadmium, and silver formed from aqueous solutions of various salts by the electrolysis at high current densities was carried out, and the formation of spongy deposits during the electrolysis of solutions of cadmium and zinc sulfate was investigated.

1. The powder-like deposits are dispersed and contain oxides, which are formed as a result of secondary oxidation processes at the cathode.
2. The approximate oxide content of the deposits, determined by a comparison of the intensity of the diffraction rings, depends mainly upon the oxidizing capacities of the anion of the salt.
3. The oxide content depends also upon the readiness of the deposited metal to become oxidized, i.e., upon its position in the electromotive series.
4. Some metals and their oxides—copper, cadmium, cuprous oxide, and zinc oxide—which enter into the composition of the deposits have greatly enlarged parameters of the crystal gratings, evidently due to the absorption of hydrogen. Zinc and silver have normal parameters.
5. The appearance of a porous structure at very low and at too high current densities is explained.

REFERENCES

- (1) ALLEN, KERSTEN, AND MAAS: C. I, 13 (1933).
- (2) FOERSTER AND GÜNTHER: Z. Elektrochem. **5**, 16 (1898); **6**, 301 (1899).
- (3) FOERSTER AND SEIDEL: Z. anorg. Chem. **14**, 106 (1897).
- (4) KILIANI AND BERG: Hüttenm. Ztg., p. 251 (1883).
- (5) KISTIAKOVSKY, BYMAKOV, AND KROTOV: Bull. acad. sci. U. R. S. S. **9**, 777 (1929).
- (6) KUDRA, O.: J. Gen. Chem. U. S. S. R. **5**, 1, 121 (1935); Mem. Inst. Chem. Kiev **1**, 81 (1934).
- (7) LUTHER, R.: Z. physik. Chem. **34**, 488 (1900); **36**, 385 (1901).
- (8) MYLIUS AND FROMM: Ber. **27**, 645 (1894).
- (9) MYLIUS AND FROMM: Z. anorg. Chem. **9**, 164 (1895).
- (10) MYLIUS AND FUNK: Z. anorg. Chem. **13**, 157 (1897).
- (11) NISSENSON AND DANEEL: Z. Elektrochem. **9**, 760 (1903).
- (12) POGGENDORF: Ann. Physik [2] **75**, 337 (1848).
- (13) SEEBORN: Trans. Faraday Soc. **29**, 825 (1933); CB. I, 193 (1934).
- (14) SIEMENS HALSKE: German patent 66,592 (1892).

THE POSTPRECIPITATION OF ZINC SULFIDE WITH MERCURIC SULFIDE¹

I. M. KOLTHOFF AND R. MOLTZAU

School of Chemistry, University of Minnesota, Minneapolis, Minnesota

Received January 10, 1936

The induced precipitation of zinc sulfide by cupric sulfide has been investigated by Kolthoff and Pearson (6). These authors pointed out that the phenomenon is not a case of coprecipitation, but one of postprecipitation. In the present study it is shown that mercuric sulfide has a much greater promoting effect on the postprecipitation of zinc sulfide than has copper sulfide. The results are not only of quantitative but also of qualitative significance. It will be shown that all or most of the zinc may be found in the precipitate of the second group when mercury is present, the acidity not too high, and filtration made not too quickly after passage of hydrogen sulfide. In addition, the mechanism of the promoted precipitation of zinc sulfide by mercuric sulfide has been studied more in detail and investigated as a function of the age and treatment of the mercuric sulfide. For a great number of details and experimental results the reader is referred to the thesis of the junior author (see footnote 1). A review of the entire subject has been published recently (5).

MATERIALS USED

All materials used were recrystallized from c.p. quality reagents and tested for purity.

When working with mercuric chloride in the presence of hydrochloric acid a white precipitate of $2\text{HgS} \cdot \text{HgCl}_2$ was first formed on passage of hydrogen sulfide, being transformed to black mercuric sulfide with more hydrogen sulfide. In order to exclude the formation of this intermediary compound, experiments were also made with solutions of mercuric perchlorate instead of mercuric chloride in sulfuric acid medium.

The hydrogen sulfide was prepared in an ordinary Kipp generator from commercial stick iron sulfide and commercial hydrochloric acid. The iron sulfide contains a considerable amount of free iron, which leads to a dilution of evolved hydrogen sulfide with hydrogen. It was found that the varia-

¹ From the experimental part of a thesis submitted by Romund Moltzau to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1935.

tion in partial pressure of the hydrogen sulfide with the strength of the acid present in the generator and the varying composition of the iron sulfide were responsible to a great extent for the difficulty experienced in obtaining reproducible results in the postprecipitation of zinc sulfide. Poor reproducibility has been noted by many workers in this field (1, 3, 6). The gas from the generator was first passed through a solution of sodium bicarbonate and then through water before entering the precipitation flasks.

PROCEDURE

Method of precipitation with hydrogen sulfide

The precipitations were carried out in 250-ml. Erlenmeyer flasks of Pyrex glass. The washed gas was led into the precipitation flasks through flexible connections allowing mechanical shaking of the solutions during continued passage of hydrogen sulfide. The electrically operated shaker employed provided a decided movement of the solutions without splashing onto the stoppers by imparting a rotary motion in the horizontal plane. Care was taken to realize as far as possible a uniform flow of gas in comparable experiments. Unless otherwise stipulated the following general procedure was observed. Before precipitation the air was expelled from the system by rapid passage of hydrogen sulfide for a period of two minutes. The gas was then bubbled through the solutions for a few minutes (usually three) accompanied by gentle shaking by hand. Thereafter continuous passage of gas was maintained over the solutions during the subsequent period of mechanical shaking.

Method of analysis

In general the following method of analysis was employed. The contents of the precipitation flasks were filtered and the precipitates immediately washed four times with cold water. The filtrates containing the washings were then boiled until free of hydrogen sulfide and, in case only small amounts of zinc were present, were evaporated to appropriate volumes. The solutions after cooling were titrated with 1/40 *M* potassium ferrocyanide solution, using diphenylamine as an internal oxidation-reduction indicator in the presence of a small amount of potassium ferricyanide. The method followed was that recommended by Kolthoff and Pearson (7).

In cases where large amounts of hydrochloric acid were present in the filtrate, most or all of it was removed by evaporation and the residue, if heated to dryness, was taken up in 10 ml. of 4 *N* sulfuric acid and diluted to an appropriate volume. In many cases the precipitates were extracted with hot or cold 3 *N* hydrochloric acid, in which instances the above procedure was followed before titration of the extracted zinc. Owing to the great resistance offered by the zinc in the precipitate to pass wholly into

solution the precipitates were often refluxed with hydrochloric acid (3 *N* or more concentrated). This treatment resulted in a considerable amount of mercury passing into solution which, if not removed, interfered with the analysis. In such cases the extraction solutions were resaturated with hydrogen sulfide and filtered if a filterable precipitate was obtained. It should, therefore, be understood that the analyses of the filtrates are accurate and the analyses of the extracts of the precipitates are less accurate, though the error due to the presence of any mercuric ion which may have been left in solution is probably in no case greater than 2 per cent.

Filterability of the precipitates

The nature of the mixed precipitates obtained by passing hydrogen sulfide through a solution containing both mercuric and zinc salts at an acidity allowing the precipitation of some zinc differs widely from that of pure mercuric sulfide. The mixed precipitate is slimy and more gelatinous and is much slower to filter though its color, even if it contains a large percentage of zinc, appears quite as black as that of pure mercuric sulfide. Upon aging, the mixed precipitates, as well as pure mercuric sulfide, are filtered more readily than in the fresh state.

EXPERIMENTAL RESULTS

Postprecipitation and no coprecipitation of zinc

Effect of acidity. In the first place it was shown that the zinc is not coprecipitated with mercuric sulfide. Mixtures of mercuric chloride and zinc sulfate in varying concentrations of hydrochloric acid and mixtures of mercuric perchlorate and zinc sulfate in dilute sulfuric acid were treated with hydrogen sulfide in such a way that a small part of the mercury remained in the solution. Upon analysis of the filtrates all of the zinc originally added was recovered, thus showing that zinc is not coprecipitated with mercuric sulfide.

The results in table 1, which are substantiated by a great number of experiments at other acidities and times of shaking, show conclusively that we are dealing with a postprecipitation of zinc sulfide on the surface of mercuric sulfide.

The increase of the postprecipitation with time as a function of the concentration of sulfuric acid in the precipitation medium is given in figure 1. The ordinate gives the percentage of zinc precipitated, the abscissa the time of shaking in hours before filtration. The results reproduced in figure 2 are of analytical significance. Curve 1 gives the amount of zinc precipitated expressed in per cent when the mercuric sulfide is precipitated in various concentrations of hydrochloric acid and filtration made as quickly as possible. Curve 2 represents the percentage of zinc precipitated at

different sulfuric acid concentrations with filtration after one hour of shaking under continuous passage of hydrogen sulfide. For the composition of the solutions see the heading of table 1.

In all cases in which the precipitation was carried out from sulfuric acid medium the experiments have been repeated with mercuric perchlorate instead of mercuric chloride. Although in the latter case no intermediate white precipitate is formed, no significant differences were found, although

TABLE 1

Postprecipitation of zinc sulfide with mercuric sulfide

25 ml. of 0.05 *M* HgCl₂, 25 ml. of 0.05 *M* ZnSO₄, and acid as noted below.

Temperature, 25°C.

EXPERIMENT NO.	TIME SHAKEN	KIND OF ACID	ACIDITY BEFORE PRECIPITATION	ZINC PRECIPITATED
	<i>minutes</i>		<i>N</i>	<i>per cent</i>
1 (Blank)*	0	H ₂ SO ₄	0.30	0
2	0	H ₂ SO ₄	0.30	65
3	30	H ₂ SO ₄	0.30	95
4 (Blank)*	30	H ₂ SO ₄	0.30	0
5	0	H ₂ SO ₄	0.80	13
6	30	H ₂ SO ₄	0.80	68
7	0	H ₂ SO ₄	1.05	15
8	30	H ₂ SO ₄	1.0	47
9	30	H ₂ SO ₄	2.0	8.0
10	60	H ₂ SO ₄	2.0	8.6
11	60	H ₂ SO ₄	4.0	0
12 (Blank)*	30	HCl	0.30	0
13	0	HCl	0.30	60
14	30	HCl	0.30	85
15	0	HCl	0.80	10.5
16	30	HCl	0.80	22
17	120	HCl	0.80	28
18	0	HCl	1.0	6.8
19	30	HCl	1.0	13
20	0	HCl	1.5	1.6
21	30	HCl	1.5	2.8
22	0	HCl	1.75	0.5
23	60	HCl	2.0	0

* The blanks contained 25 ml. of water in place of 25 ml. of 0.05 *M* HgCl₂.

under all conditions slightly more zinc was postprecipitated by mercuric sulfide obtained from the perchlorate. The difference may be attributed to a difference in particle size of the mercuric sulfide obtained by precipitation of the chloride and perchlorate respectively.

Figure 3 gives the percentage of zinc postprecipitated from a medium 2 *N* in sulfuric acid after long periods of standing under an atmosphere of hydrogen sulfide at room temperature. The original mixture contained

25 ml. of 0.05 *M* mercuric chloride, 25 ml. of 0.05 *M* zinc sulfate, and 10 ml. of 12.0 *N* sulfuric acid, and was kept saturated with hydrogen sulfide by replenishing every twelve hours for the first four days by passage of hydrogen sulfide above the solution for five minutes. Thereafter the gas phase was replenished every two days. In the absence of mercuric sulfide no precipitate of zinc sulfide was formed after a month of standing under like conditions.

The effect of varying the ratio of mercury to zinc at relatively low acidities is shown in table 2. In table 3 the results are reported for a medium which was 2 *N* in sulfuric acid.

Unity in the expression of ratio represents 1.25 millimoles of mercury and zinc, respectively (25 ml. of 0.05 *M* solution).

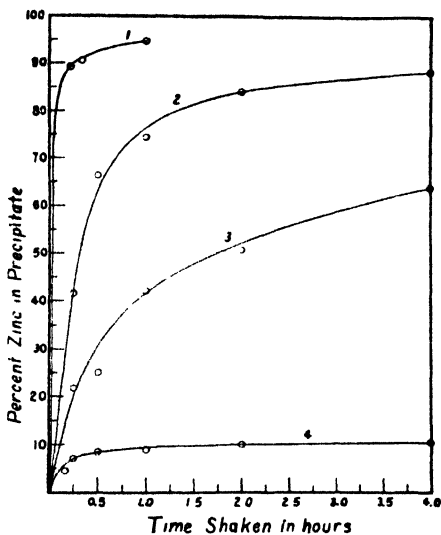


FIG. 1

FIG. 1. Time effect at various acidities. Acidity (sulfuric acid) before precipitation: curve 1, 0.35 *N*; curve 2, 0.77 *N*; curve 3, 1.31 *N*; curve 4, 2.0 *N*.

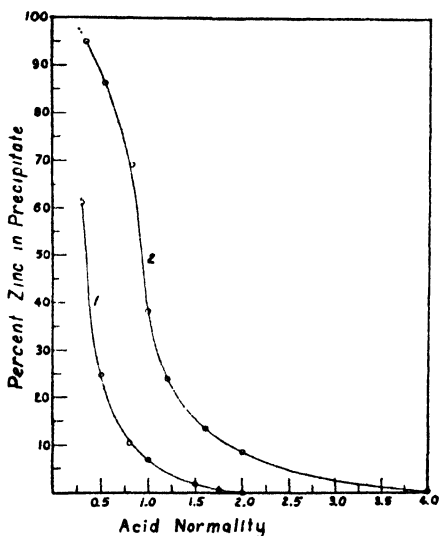


FIG. 2

FIG. 2. Effect of acidity

In table 4 some results are given on the disappearance of zinc from a very dilute zinc solution at a high acidity after various times of standing with freshly precipitated mercuric sulfide.

Effect of partial pressure of hydrogen sulfide upon the postprecipitation of zinc sulfide

In the following experiments (see table 5) the hydrogen sulfide was diluted with carbon dioxide before entering the precipitation flasks. In the blanks a stream of pure hydrogen sulfide having the same rate of flow (about one bubble per second) as the stream of hydrogen sulfide uniting

with carbon dioxide in the experiments was used. It took three to five minutes to precipitate the mercury completely using the diluted gas; less time was needed using the slow stream of pure hydrogen sulfide.

Effect of temperature

Those experiments (see table 6) in which the temperature is described as "hot" were heated over a burner until bubbles began to break the surface of the solution. They were then immediately attached to the source of hydrogen sulfide in parallel with a corresponding experiment run at room temperature. Hydrogen sulfide at room temperature was passed in above the solutions for one minute and bubbled through the solutions for three minutes in accordance with the usual method of precipitation. No further heat was applied after the initial heating and hence the flasks slowly cooled during the period of shaking, which was conducted under constant

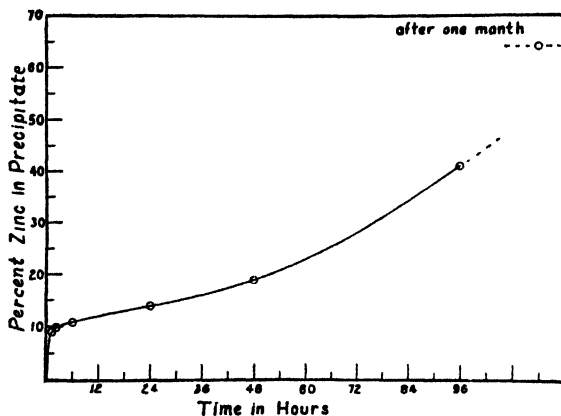


FIG. 3. Time effect at an acidity of 2.0 *N* in sulfuric acid

passage of the gas. Blanks were run which contained 25 ml. of water in place of the mercuric solution.

The "wall effect" mentioned in the "remarks" after experiment No. 6 is evidenced by a deposit of zinc sulfide on the walls of the flask. It is formed during the period of shaking. Avoidance of this effect is aided by the use of flasks which are well cleaned and free of scratches or rough surfaces.

Similar experiments were made in 0.35 *N* sulfuric acid, giving results strictly concordant with those in table 6.

Effect of aging of mercuric sulfide upon the promotion of precipitation of zinc sulfide

A series of experiments was made in which the mercuric sulfide for each individual experiment was precipitated from 25 ml. of 0.05 *M* mercuric chloride at an acidity of 0.73 *N* hydrochloric acid. The precipitate was

TABLE 2

The effect of varying the ratio of mercury to zinc at relatively low acidities

Room temperature. The total volume of solution in each experiment was approximately 55 ml.

EXPERIMENT NO.	ACIDITY BEFORE PRECIPITATION	TIME SHAKEN	RATIO Zn Hg	ZINC IN FILTRATE IN PER CENT	ZINC IN PRECIPITATE IN PER CENT
1 (Blank)*	0.35 N (H ₂ SO ₄)	0		100 0	0
2	0.35 N (H ₂ SO ₄)	0	1:2	49 6	50 4
3	0.35 N (H ₂ SO ₄)	0	1:1	57.6	42 4
4	0.35 N (H ₂ SO ₄)	0	1:1/2	60 4	39.6
5	0.35 N (H ₂ SO ₄)	10 mins.	1:2	8 3	91.7
6	0.35 N (H ₂ SO ₄)	10 mins.	1:1	10 7	89 3
7	0.35 N (H ₂ SO ₄)	10 mins.	1:1/2	15 9	84 1
8	0.55 N (H ₂ SO ₄)	1 hr.	1:1/10	27 8	72 2
9	0.55 N (H ₂ SO ₄)	1 hr.	1:1/100	81 8	18 2
10	0.55 N (H ₂ SO ₄)	1 hr.	1:1/750	96 0	4 0
11	0.20 N (H ₂ SO ₄)	1 hr.	1:1/10	0 0	100.0
12	0.20 N (H ₂ SO ₄)	1 hr.	1:1/100	21 0	79 0
13	0.20 N (H ₂ SO ₄)	1 hr.	1:1/750	54 6	45 4
14 (Blank)*	0.20 N (H ₂ SO ₄)	1 hr.		98 0	2.0

* The blanks contained no mercury salt.

TABLE 3

Effect of ratio at high acidity (2 N in sulfuric acid)

Room temperature. The total volume of solution in each experiment was 60 ml.

EXPERIMENT NO.	TIME SHAKEN	RATIO Zn. Hg	ZINC IN FILTRATE IN PER CENT	ZINC IN PRECIPITATE IN PER CENT
1	2 hrs.	1:4	74 6	25 4
2	2 hrs.	1:2	81 9	18.1
3	2 hrs.	1:1	90 9	9 1
4	2 hrs.	2:1	86 8	13 2
5	2 hrs.	1/5:1	92.7	7.3
6	1 hr.	1:4	80.5	19 5
7	1 hr.	1:2	86.7	13.3
8	1 hr.	1:1	93 2	6 8
9	1 hr.	1:1/2	95 5	4.5
10	1 hr.	2:1	87 4	12 6
11	1 hr.	1/2:1	90 5	9 5
12	1 hr.	1/5:1	95 7	4.3
13	1 hr.	2/5:2	89 5	10.5
14	30 mins.	2/5:2	93 5	6 5
15	30 mins.; stood stoppered 4 days	2/5:2	81 7	18.3

allowed to age in this medium saturated with hydrogen sulfide. After the time indicated in the table as "time of aging", 25 ml. of 0.05 *M* zinc sulfate solution was added and immediately thereafter hydrogen sulfide was passed over the solution for one minute and bubbled through for two minutes. The contents of the precipitation flask were then shaken under continuous

TABLE 4

Time effect at an acidity of 2 N in sulfuric acid employing very dilute zinc solution

Contents of flasks before precipitation: 25 ml. of 0.05 *M* HgCl_2 , 25 ml. of 0.01 *M* ZnSO_4 , 10 ml. of 12.0 *N* H_2SO_4 (molarity $\text{ZnSO}_4 = 0.00417$). Room temperature. Each experiment was shaken for one hour under continuous passage of hydrogen sulfide after the three-minute precipitation period and thereafter allowed to stand under an atmosphere of hydrogen sulfide for the period of time given in the table before filtration

EXPERIMENT NO.	TIME OF STANDING	ZINC IN FILTRATE IN PER CENT	ZINC IN PRECIPITATE IN PER CENT
1	0	90.0	10.0
2	0	90.8	9.2
3	1 day	89.0	11.0
4	1 day	89.4	10.6
5	3 days	90.1	9.9
6	3 days	90.7	9.3

TABLE 5

Effect of the partial pressure of hydrogen sulfide

25 ml. of 0.05 *M* HgCl_2 , 25 ml. of 0.05 *M* ZnSO_4 , and a volume of 4 *N* H_2SO_4 required to give the acidities indicated in the table. Room temperature

EXPERIMENT NO.	ACIDITY BEFORE PRECIPITATION	COMPOSITION OF GAS STREAM APPROXIMATE RATIO $\text{H}_2\text{S} : \text{CO}_2$	TIME SHAKEN	ZINC IN FILTRATE IN PER CENT
1	1.01 <i>N</i> in H_2SO_4	Pure H_2S	1 hr.	62.7
2	1.01 <i>N</i> in H_2SO_4	1:10	1 hr.	99.1
3	1.01 <i>N</i> in H_2SO_4	1:20	1 hr.	100.0
4	0.55 <i>N</i> in H_2SO_4	Pure H_2S	30 mins.	30.4
5	0.55 <i>N</i> in H_2SO_4	1:10	30 mins.	91.3
6	0.55 <i>N</i> in H_2SO_4	1:20	30 mins.	97.8
7	0.30 <i>N</i> in H_2SO_4	Pure H_2S	30 mins.	8.1
8	0.30 <i>N</i> in H_2SO_4	1:10	30 mins.	87.8
9	0.30 <i>N</i> in H_2SO_4	1:20	30 mins.	96.5

passage of hydrogen sulfide for ten minutes, filtered, the precipitate washed four times with cold water, and the filtrates analyzed for zinc. Another series was also made in which the mercuric sulfide was precipitated from mercuric chloride solution without addition of acid. After the period of aging, acid and zinc sulfate solution were added in the order named and

the experiments further conducted as described above. The results are given in table 7. The acidities listed are uncorrected for acid set free by the reaction.

Another set of experiments was carried out in which the mercuric sulfide was precipitated in 0.75 *N* hydrochloric acid at the boiling temperature. No further heating took place after precipitation, and the precipitate and supernatant liquid were allowed to cool down to room temperature. Zinc solution was added after various time intervals. The results obtained

TABLE 6

Effect of temperature

25 ml. of 0.05 *M* HgCl_2 , 25 ml. of 0.05 *M* ZnSO_4 , and 8 ml. of 3.95 *N* H_2SO_4 . Acidity before precipitation was 0.55 *N* in H_2SO_4

EXPERIMENT NO.	TIME SHAKEN	TEMPERATURE OF PRECIPITATION	ZINC in FILTRATE	REMARKS
	<i>minutes</i>	<i>°C.</i>	<i>per cent</i>	
1	0	Hot	85 7	The white precipitate ($2\text{HgS} \cdot \text{HgCl}_2$) persisted for one minute before becoming black
2	0	27	72 3	No white precipitate was observed
3	0	Hot	79 6	White precipitate persisted for 30 seconds. H_2S passage more rapid in experiments 3 and 4 than in 1 and 2
4	0	27	57.6	No white precipitate was observed
5	10	Hot	36 4	
6 (Blank)	30	Hot	99 5	No Hg present. Some wall effect, but the solution was entirely clear at the end of the period of shaking
7	10	Hot	38 3	
8	10	27	37 8	
9	20	Hot	22 4	
10	20	27	21 1	
11	20	Hot	19.5	
12	20	27	20 4	

were practically identical with those in the first part of table 7, showing that the temperature at which the mercuric sulfide is precipitated from hydrochloric acid medium has no appreciable effect upon its ability to promote the precipitation of zinc sulfide. However, if the mercuric sulfide is allowed to age at higher temperatures for longer times its promoting effect upon the precipitation of zinc sulfide decreases more rapidly than when aged at room temperatures. Precipitates of mercuric sulfide obtained from mercuric perchlorate behaved qualitatively in the same way as those from mercuric chloride.

A great number of experiments were carried out in which the mercuric sulfide was precipitated and aged in 3.5 *N* sulfuric acid before the addition of zinc solution, the final acidity being 2 *N*. Under these conditions a short time of aging had relatively a much greater effect upon the speed of disappearance of zinc from the solution than when precipitation was conducted at lower acidities. This may be seen from the following example:

Age of HgS (minutes).....	0.5	2	5	10	60	120
Zinc in precipitate in per cent.....	9	7	5.5	4.5	2.4	2.0

The difference between these results and those in table 7 are attributed to the fact that in strongly acid medium little, if any, precipitation but only adsorption of zinc sulfide takes place during relatively short times of contact. At lower acidities a primary adsorption takes place with an additional precipitation of zinc sulfide. The latter, once formed, promotes its own precipitation.

TABLE 7

Effect of aging of mercuric sulfide at room temperature upon precipitation

HgS AGED IN 0.73 <i>N</i> HCl				HgS AGED IN NEUTRAL MEDIUM		
Experiment No.	Acidity after addition of zinc solution	Time of aging of HgS	Zinc in the precipitate in per cent	Acidity after addition of zinc solution	Time of aging of HgS	Zinc in the precipitate in per cent
1	0.42 <i>N</i> in HCl	0	38	0.42 <i>N</i> in HCl	0	29
2	0.42 <i>N</i> in HCl	20 mins.	33			
3	0.42 <i>N</i> in HCl	30 mins.	32			
4	0.42 <i>N</i> in HCl	1 day	20	0.42 <i>N</i> in HCl	1 day	10
5	0.42 <i>N</i> in HCl	4 days	18	0.42 <i>N</i> in HCl	4 days	5
6				0.86 <i>N</i> in H ₂ SO ₄	0	21
7				0.86 <i>N</i> in H ₂ SO ₄	1 day	11

Extractability of the zinc from the mixed precipitate

By an extraction with 3 *N* hydrochloric acid at room temperature it was found impossible to remove all the zinc from the mixed precipitate. By refluxing the precipitate with 3 *N* hydrochloric acid complete extraction of the zinc was possible. However, with such drastic treatment relatively large amounts of mercuric sulfide go into solution as well and a subsequent separation is necessary before the zinc can be determined. Complete extraction of the zinc was made with less difficulty when the mercuric sulfide was allowed to age before it exerted its promoting effect upon the precipitation of zinc sulfide. An explanation of this behavior is given in the discussion of the results.

As an illustration a few data are reported in table 8. A great number of other examples of cold and hot extractions are reported in the thesis of

R. Moltzau (see footnote 1). In the following experiments the mercuric sulfide precipitated from neutral solution (25 ml. of 0.05 *M* mercuric chloride) was aged under the supernatant liquid saturated with hydrogen sulfide in tightly stoppered Erlenmeyer flasks. The gas in the flasks was replenished with hydrogen sulfide every two days of the period of aging. Experiments were run in pairs, one member of each pair containing the aged precipitate and the other a freshly precipitated product. After addition of the proper amount of acid and 25 ml. of 0.05 *M* zinc sulfate

TABLE 8
Extractability of zinc with hot 3 N hydrochloric acid

EXPERIMENT NO.	ACIDITY (H ₂ SO ₄)	TIME SHAKEN	AGE OF HgS	ZINC in FILTRATE	100 PER CENT — ZINC IN FILTRATE = ZINC IN PPT.	METHOD OF EXTRAC- TION	ZINC EX- TRACTED	TOTAL ZINC RE- COVERED
	<i>N</i>			<i>per cent</i>	<i>per cent</i>		<i>per cent</i>	<i>per cent</i>
Blank								
1	0 50	1 hr.	No HgS	100 0	0			
2	0 50	1 hr.	3 weeks	91 5	8 5	a	8 5	100 0
3	0 50	1 hr.	Fresh	15 6	84 4	a	81 4	97 0
4	0 66	45 mins.	2 weeks	97 6	2 4	b	2 0	99 6
5	0 66	45 mins.	Fresh	85 9	14 1	b	11 2	97 1
6	0 66	45 mins.	2 weeks	97 0	3 0	d	2 5	99 5
7	1 0	45 mins.	2 weeks	99 3	0 7	c	0 42	99 7
8	1 0	45 mins.	Fresh	91 9	8 1	c	4 7	96 6
9	1 0	2 hrs.	3 weeks	87 8	12 2	d	12 2	100 0
10	1 0	2 hrs.	Fresh	46 0	54 0	d	52 6	98 6

Method a. The precipitate was placed in a beaker with 25 ml. of hot 3 *N* hydrochloric acid. This mixture stood with occasional stirring for fifteen minutes, was filtered and the residue washed three times with cold 3 *N* hydrochloric acid and four times with cold water.

Method b. Same as method a except that the acid and the precipitate were in contact for twenty minutes rather than for fifteen minutes.

Method c. Same as methods a and b, except that period of contact was ten minutes.

Method d. The precipitate on the filter was washed ten times (5-ml. portions) with hot 3 *N* hydrochloric acid and four times with cold water.

solution, hydrogen sulfide was again bubbled through the solution for two minutes, and thereafter the contents of the flasks were shaken under continuous passage of hydrogen sulfide for the time noted. The acidity given is that of the solution after addition of the zinc solution uncorrected for acid liberated by the reaction.

Inhibition of postprecipitation of zinc sulfide

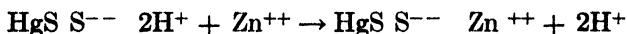
(a) *By replacing adsorbed hydrogen sulfide.* It was shown by Kolthoff and Pearson (6) that organic substances containing polar sulfur groups

can replace part of the adsorbed hydrogen sulfide from the surface of cupric sulfide, thus causing an inhibition of the postprecipitation of zinc sulfide. Similar experiments were carried out in the present study with thiourea and cystine as inhibitors. In both cases it was found that the organic substance added retarded the postprecipitation of zinc sulfide with mercuric sulfide.

Experiments have also been performed in which the precipitation of mercuric sulfide was carried out in the presence of a layer of an immiscible liquid such as ether or carbon disulfide. In general a pronounced retarding effect upon the postprecipitation of zinc sulfide was found. This may be explained partly by the fact that the mercuric sulfide is more or less isolated from the aqueous solution by the second layer of organic liquid.

(b) *By replacing adsorbed zinc ions.* Before precipitation of zinc sulfide on the surface of mercuric sulfide occurs, an adsorption of zinc ions with the sulfide ions takes place. Ions competing with the zinc ions for adsorption with the sulfide ions will inhibit the postprecipitation of zinc sulfide.

In the first place it was shown that zinc ions are adsorbed by mercuric sulfide containing some adsorbed hydrogen sulfide.



A fresh precipitate of mercuric sulfide from 25 ml. of 0.05 *M* mercuric chloride solution was washed with cold water until the test for sulfide and chloride in the filtrate was very faint. The precipitate was then shaken with 25 ml. of 0.005 *M* zinc sulfate and the amount of hydrogen ions liberated and zinc adsorbed was determined by titrating the filtrate with sodium hydroxide to the methyl red end point and then with ferrocyanide to determine the zinc content. In all cases the amount of acid liberated was found equivalent to the amount of zinc adsorbed.

Milliequivalents of acid liberated.....	0.029	0.025	0.022	0.016
Milliequivalents of zinc adsorbed.....	0.0285	0.0245	0.0220	0.0158

The results show conclusively that the adsorption of zinc ions is to be attributed to an exchange with hydrogen ions on the surface of the mercuric sulfide.

It was further shown that strychnine ions give a similar exchange. The strychnine was determined gravimetrically by the ferrocyanide method as recommended by Kolthoff and Lingane (4). Working with a washed mercuric sulfide precipitate, a complete exchange between the adsorbed hydrogen ions and strychnine ions was found in a solution which was 0.005 *M* in strychnine sulfate. It is suggested that a strychnine salt may be used in the determination of the amount of hydrogen sulfide adsorbed by a metal sulfide precipitate. In stronger acid medium it will be harder to replace the hydrogen ions by zinc or strychnine ions, since the effect depends

upon a competition between hydrogen ions and the other ions to be adsorbed.

In weakly and strongly acid medium strychnine inhibits the postprecipitation of zinc sulfide by mercuric sulfide. A few examples of the effect in 1.4 *N* sulfuric acid are given in table 9. The air was expelled from above the solution by a two-minute passage of hydrogen sulfide followed by a three-minute period during which the gas was bubbled through the contents of the precipitation flask. Thereafter the mixture was shaken under continuous passage of hydrogen sulfide over the solution for thirty minutes. Filtration and washing were conducted as usual and the filtrates analyzed for zinc content after destroying the strychnine with bromine.

In very weakly acid medium, where the only hydrogen sulfide present was that adsorbed on the mercuric sulfide, aluminum ions were found to exert a slight replacing effect upon the adsorption of zinc ions. In more strongly acid medium, however, the aluminum did not exert an inhibiting effect upon the postprecipitation of zinc sulfide.

TABLE 9

Inhibition of postprecipitation in the presence of strychnine

25 ml. of 0.05 *M* HgCl₂, 10 ml. of 12.06 *N* H₂SO₄, 25 ml. of 0.025 *M* strychnine acid sulfate (or 25 ml. of 0.025 *N* H₂SO₄ in blanks), and 25 ml. of 0.05 *M* ZnSO₄

CONDITION	ZINC IN FILTRATE	ZINC IN PRECIPITATE
	<i>per cent</i>	<i>per cent</i>
Strychnine present . . .	93 7	6 3
Strychnine present.	94 0	6 0
No strychnine present . . .	84 5	15 5
No strychnine present	83 2	16 8

DISCUSSION OF THE RESULTS

1. From the analytical viewpoint it is of interest to mention that at acidities at 0.3 *N* sulfuric acid 65 per cent of the zinc was found in the mercuric sulfide precipitate when filtration was made immediately after a three-minute period of precipitation. Upon waiting for thirty minutes only 5 per cent of the zinc originally present was recovered in the filtrate. Even when precipitated from 1 *N* sulfuric acid the mercuric sulfide contains about 15 per cent of the zinc present upon rapid filtration and about 8 per cent when precipitated from 1 *N* hydrochloric acid. In order to get a quantitative separation the precipitation should be made in a solution 4 *N* with regard to sulfuric acid or 2 *N* with respect to hydrochloric acid. At the same acid concentration hydrochloric acid is more effective in retarding the precipitation of zinc sulfide than is sulfuric acid, since the activity of the hydrogen ions in the case of the former is much greater. The difference in behavior of hydrochloric and sulfuric acids is clearly

shown in figure 4. The ordinate represents the amount of zinc precipitated after shaking for thirty minutes under hydrogen sulfide (for conditions see table 1), whereas the abscissa indicates the normality of the acid.

2. The results in table 5 show that the extent of postprecipitation is decreased materially when the hydrogen sulfide pressure is diminished. Whereas 37 per cent of the zinc was postprecipitated at an acidity of 1 *N* in sulfuric acid after a one-hour period of shaking, only 0.9 per cent was postprecipitated when the gas was diluted ten times with carbon dioxide and no zinc was found in the precipitate with a twentyfold dilution (experiments 1 to 3, table 5). At lower acidities the differences are still more striking. These results are of analytical importance, since it should be

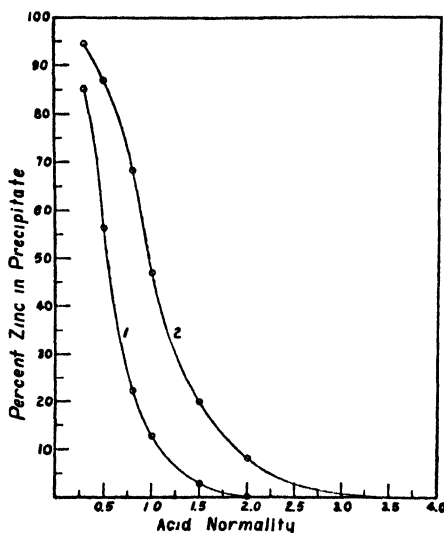


FIG. 4. Effect of acidity: effect of hydrochloric acid versus that of sulfuric acid. Curve 1, hydrochloric acid medium; curve 2, sulfuric acid medium.

possible to obtain satisfactory separations in those cases in which precipitation with hydrogen sulfide under normal pressure gives serious errors as a result of postprecipitation. The effect of the partial pressure of the gas also explains why results obtained in these postprecipitation studies frequently are irreproducible if the ratio of hydrogen sulfide to hydrogen in the gas produced in the generator varies. Moser and Behr (8) found that increased gas pressure promotes the speed and completeness of precipitation of zinc and other sulfides and made an analytical application thereof.

3. The results in table 2 show that at relatively low acidities very small amounts of mercuric sulfide cause the precipitation of appreciable quantities of zinc sulfide (see experiments 11 and 15), the amount of zinc precipitated being far greater than corresponds to the formation of mixed sulfides

in the sense of Feigl (2). Evidently there is no one-to-one proportionality between the extent to which zinc sulfide is carried down and the amount of mercuric sulfide present. The primary reaction taking place is an adsorption of zinc sulfide on the surface of mercuric sulfide. The zinc sulfide thus formed exerts a self-promoting action on its own precipitation (3). A similar effect may be attributed to the mercuric sulfide, since it is isomorphous with zinc sulfide. When precipitation takes place at a high acidity (2 *N* in sulfuric acid) at a given concentration of zinc salt the amount of zinc found in the precipitate approximates, over a limited range, a one-to-one proportionality with the amount of mercuric sulfide present. From the results in table 3 it may be concluded that at high acidities during the first two hours we are dealing primarily with an adsorption of zinc sulfide on the surface of mercuric sulfide, and that postprecipitation is of secondary importance for relatively short periods of time after precipitation of the mercuric sulfide. Upon longer times of standing a slow postprecipitation of zinc sulfide occurs. In this way the shape of the curve in figure 3 is easily explained. The initial rapid rise in the curve is attributed to an adsorption of zinc sulfide, which is followed by a slow postprecipitation of zinc sulfide represented by the flatter portion of the curve. The interpretation is substantiated by the results of table 4. In these experiments the zinc sulfate concentration was five times smaller than in those reported in table 3. Comparison of experiments 1 and 2 of table 4 with 6 and 7 of table 3 shows that the same percentage of zinc present in the solution was adsorbed by the mercuric sulfide, although in the latter case the total zinc concentration was five times greater than in the former. There is a competition between the zinc and hydrogen ions for adsorption on the surface of the mercuric sulfide. At a given hydrogen-ion concentration the ratio $\left(\frac{\text{Zn}^{++}}{\text{H}^{+}}\right)$ adsorbed is constant. Thus when the zinc concentration is decreased five times the percentage of zinc adsorbed from the solution remains unchanged. Whereas in the experiments reported in table 3 a slow postprecipitation of zinc sulfide was found upon longer times of standing, no indication of a *precipitation* of zinc sulfide was found at a fivefold smaller concentration of zinc salt in the solution after three days of standing at an acidity of 2 *N* sulfuric acid. At this high acidity and low zinc concentration the solution is no longer supersaturated with regard to zinc sulfide, and no postprecipitation can take place. In this way it is possible to interpret the entire mechanism of the adsorption and postprecipitation of zinc sulfide by mercuric sulfide.

4. One of the most striking and interesting results of this study is that a postprecipitation of zinc sulfide was found in a medium which was 2 *N* sulfuric acid (table 3 and also figure 3). If an excess of freshly precipitated zinc sulfide was added to a solution of zinc sulfate in 2 *N* sulfuric acid of

the same composition as the supernatant liquid in the postprecipitation studies after the precipitation of the mercury and saturation with hydrogen sulfide, it was found that part of the zinc sulfide went into solution. In spite of this fact a slow precipitation of zinc sulfide occurs from the same medium when mercuric sulfide is present as the solid body. The apparent contradiction to the mass action law is explained by the fact that the solubility of zinc sulfide depends greatly upon the manner of its preparation and its age. The effect of aging of zinc sulfide upon its solubility is clearly demonstrated by the experiments reported in table 10.

TABLE 10
Decrease of solubility of zinc sulfide upon aging

EXPERIMENT NO.	REAGENTS	H ₂ SO ₄ CONCENTRATION IN FINAL MIXTURE (NORMALITY)	TIME SHAKEN	Zn ORIGINALLY IN SOLUTION (MOLARITY)	FINAL Zn IN SOLUTION (MOLARITY)
Blank 1	25 ml. of 0.05 <i>M</i> ZnSO ₄ , 25 ml. of 2.0 <i>N</i> H ₂ SO ₄	1 0	2 hrs.	0 0250	0 0250
2	Same as No. 1 plus solid ZnS (fresh)	1 0	2 hrs.	0 0250	0 0223
3	25 ml. of 0.05 <i>M</i> HgCl ₂ , 25 ml. of 0.05 <i>M</i> ZnSO ₄ , 10 ml. of 12.0 <i>N</i> H ₂ SO ₄	2 0	2 hrs.	0 0208	0 0189
4	Same as No. 3 and No. 4 plus excess solid ZnS (fresh)	2 0	2 hrs.	0.0208	0 0358
5	60 ml. of 2.0 <i>N</i> H ₂ SO ₄ saturated with H ₂ S. Excess solid ZnS (fresh)	2 0	6 hrs.	0	0.0354
6	60 ml. of 2.0 <i>N</i> H ₂ SO ₄ saturated with H ₂ S plus large excess ZnS (aged)	2.0	3 hrs.	0	0 0049
7	As 6. Small excess ZnS (aged)	2 0	1 5 hrs.	0	0.0050
8	25 ml. of 0.05 <i>M</i> ZnSO ₄ , 25 ml. of water, 10 ml. of 12.0 <i>N</i> H ₂ SO ₄ , excess solid ZnS (aged)	2 0	Stood 1 month	0 0208	0 0052
Blank 9	25 ml. of 0.05 <i>M</i> ZnSO ₄ , 25 ml. of water, 10 ml. of 12.0 <i>N</i> H ₂ SO ₄	2 0	Stood 1 month	0 0208	0 0208

The solid zinc sulfide designated as the fresh product was prepared by precipitation from a 0.1 *M* solution of zinc sulfate by the action of hydrogen sulfide. The acidity before precipitation was 0.08 *N* in sulfuric acid. After a fifteen-minute period of precipitation the sulfide was filtered off, washed several times with water and added in a moist condition to the contents of the precipitation flasks. The aged product employed was formed from a solution of zinc sulfate having an acidity before precipitation of 0.2 *N* in sulfuric acid. The precipitate was allowed to age in the mother liquor saturated with hydrogen sulfide for one month before use. As in the case

of the fresh product the aged precipitate was added to the contents of the precipitation flasks in a moist condition. The work was conducted at room temperature. The acidity given is, as usual, uncorrected for acid liberated or used up by the reaction taking place. The procedure followed consisted of bubbling hydrogen sulfide through the mixture of solutions indicated for a period of three minutes after expulsion of air. Thereafter the contents of the flasks were shaken with continuous passage of hydrogen sulfide over the solutions for the time indicated in the table. In experiments 8 and 9 the solutions were kept saturated with hydrogen sulfide by frequent replenishments of the gas phase throughout the month of standing. In case solid zinc sulfide was added, addition was made after an interval of shaking sufficiently long (fifteen minutes) to insure thorough saturation of the solution with hydrogen sulfide. At the end of the period of shaking the contents of the flasks were filtered, the precipitates washed four times with cold water, and the filtrates analyzed for zinc in the usual manner.

It appears from the table that the solutions employed (0.02 *M* with respect to zinc salt, 2.0 *N* in sulfuric acid, saturated with hydrogen sulfide), while undersaturated with respect to the very small and imperfectly crystalline particles of freshly precipitated zinc sulfide, were supersaturated with respect to the aged product. The difference in solubility, in 2 *N* sulfuric acid saturated with hydrogen sulfide, of the two products is very marked, being in the neighborhood of 0.005 *M* for the aged precipitate as compared to 0.035 *M* in the case of the fresh product. Had the decrease in solubility with aging been due to only a partial change to a more insoluble form we should expect to find a greater solubility of zinc sulfide in those experiments where a large excess of the aged product was present than in those where only a small excess was present. Comparison of experiments No. 6 and No. 7, corroborated by duplicate experiments not shown in the table, shows that such is not the case. X-ray evidence gave no indication that the bulk of the precipitate changes crystal modification on aging, but did show an increase in the perfection of its crystalline state. The postprecipitation of zinc sulfide by mercuric sulfide in a medium of 2 *N* sulfuric acid is extremely slow. Apparently the zinc sulfide is precipitated in the aged, less soluble form. Even after a month of contact with mercuric sulfide equilibrium had not as yet been reached when the original zinc sulfate concentration in the mixture was 0.02 molar. If the original concentration of zinc salt was decreased to 0.004 molar no postprecipitation occurred even after long times of standing, since the solubility of well-aged zinc sulfide is greater than corresponds to this zinc concentration in 2 *N* sulfuric acid saturated with hydrogen sulfide.

5. The postprecipitation of zinc sulfide can be inhibited by making use of two different principles: (a) by the replacement of the adsorbed hydro-

gen sulfide on mercuric sulfide by an organic substance containing polar sulfur groups (a similar inhibiting effect was found by Kolthoff and Pearson (6) in working with the system copper sulfide–zinc sulfide), and (b) by a replacement of the adsorbed zinc ions by other cations. It has been shown that strychnine ions are fairly effective in this respect at various acidities (table 9). Aluminum ions, on the other hand, have only a slight replacing effect upon the zinc ions and exert no inhibiting effect upon the postprecipitation of zinc sulfide.

6. The promoting effect of mercuric sulfide upon the precipitation of zinc sulfide decreases when the mercuric sulfide is aged. Upon aging in the supernatant liquid an agglomeration of the particles occurs, resulting in a decrease of the surface and therefore, also, of the promoting effect upon the precipitation of zinc sulfide. In addition to a coarsening of the particles of mercuric sulfide, a transformation of the black, cubic form of metacinnabar into the red, trigonal form of cinnabar occurs upon aging. The speed of transformation is fairly great at low acidities and decreases with increasing acidity of the supernatant liquid. This explains why mercuric sulfide aged in neutral medium exerts less promoting effect upon the postprecipitation of zinc sulfide than that aged in acid medium for the same length of time (table 7). The speed of transformation of the black into the red form is favored very strongly by an increase in temperature. For this reason aging of the mercuric sulfide at higher temperatures decreases its promoting effect on the postprecipitation of zinc sulfide much more than aging for the same length of time at room temperature.

7. When the mixture of mercuric chloride and zinc salt is precipitated with hydrogen sulfide at higher temperatures and filtration made after the three-minute precipitation period, less zinc was found to be postprecipitated than when treated with hydrogen sulfide at room temperature (table 6). If, however, the solutions were allowed to cool down during a period of shaking under hydrogen sulfide pressure, the final result was about the same as for those experiments carried out entirely at room temperature.

8. In the experimental part of this paper it has been mentioned that zinc sulfide postprecipitated with fresh mercuric sulfide cannot be completely removed from the precipitate by a continuous extraction with 3 *N* hydrochloric acid at room temperature. Complete extraction is easier from precipitates which are formed with aged mercuric sulfide than from those formed by precipitation from solutions containing both metallic ions or from those obtained by using freshly precipitated mercuric sulfide. Apparently the zinc sulfide is intimately associated with the mercuric sulfide in the mixed precipitate, although the latter when first formed contains no zinc. The difficulty with which extraction of the zinc is made from the mixed precipitate suggests that it is present in the form of a mixed crystal.

X-ray studies reported in a previous paper (7a) indicated that a limited mixed crystal formation had occurred. The zinc sulfide then enters the black mercuric sulfide lattice after the latter has been formed. This penetration takes place most easily into freshly precipitated mercuric sulfide and only with great difficulty, if at all, in case of a well-aged product, thus accounting for the differing ease of extractability of the zinc from various types of precipitates. When dealing with fresh precipitates the penetration takes place to a maximum extent very quickly. Inasmuch as transformation to the trigonal form occurs to a large extent in all of the well-aged precipitates of mercuric sulfide, it is not possible to state definitely whether or not penetration is possible in a well-aged mercuric sulfide which has retained its cubic form. Experiments carried out with mercuric sulfide aged in strongly acid medium, in which the transformation to the red form is very slow, indicate that there may be slow penetration into well-aged products providing they consist of the metacinnabar form. It seems fairly conclusive that no penetration occurs in the case of the red hexagonal form—in other words, no mixed crystals of hexagonal habit form, although the red mercuric sulfide promotes the precipitation of zinc sulfide. It may be mentioned that the subsequent mixed crystal formation of postprecipitated zinc sulfide with mercuric sulfide is of secondary consideration with regard to the general problem of postprecipitation of zinc.

SUMMARY

1. Mercuric sulfide promotes the precipitation of zinc sulfide from acid medium. There is no coprecipitation, but the phenomenon constitutes a typical case of postprecipitation.

2. The promoting effect of mercuric sulfide upon the postprecipitation of zinc sulfide is much more pronounced than that of cupric sulfide. Even traces of mercuric sulfide have a distinct effect.

3. The postprecipitation is explained by a primary adsorption of zinc sulfide on the mercuric sulfide with subsequent precipitation of the latter. Substances replacing adsorbed hydrogen sulfide or ions competing with zinc ions in their adsorption as counter ions inhibit the postprecipitation.

4. A very slow postprecipitation occurs at an acidity as high as 2 *N* in sulfuric acid, although freshly precipitated zinc sulfide would dissolve at this acidity. It has been shown that at this high acidity the zinc sulfide is postprecipitated in the aged, less soluble form.

5. With aging of the mercuric sulfide its promoting effect upon the postprecipitation decreases. This is partly explained by an agglomeration of the particles, but also by a transformation of the metacinnabar to the cinnabar form. The temperature at which the mercuric sulfide is precipitated has little effect upon its ability to promote the precipitation of zinc sulfide.

6. Zinc sulfide postprecipitated with fresh mercuric sulfide cannot be completely extracted from the precipitate with 3 *N* hydrochloric acid at room temperature. The postprecipitated zinc sulfide penetrates the lattice of the cubic mercuric sulfide, giving rise to a limited mixed crystal formation.

7. The extent of postprecipitation diminishes greatly with decreasing partial pressure of hydrogen sulfide.

REFERENCES

- (1) BRAITHWAITE, L. T.: Thesis, Columbia University, 1934.
- (2) FEIGL, F.: *Z. anal. Chem.* **65**, 25 (1924).
- (3) GLIXELLI, S.: *Z. anorg. Chem.* **55**, 297 (1907).
- (4) KOLTHOFF, I. M., AND LINGANE, J. J.: *J. Am. Pharm. Assoc.* **23**, 302 (1934).
- (5) KOLTHOFF, I. M., AND MOLTZAU, R.: *Chem. Rev.* **17**, 293 (1935).
- (6) KOLTHOFF, I. M., AND PEARSON, E. A.: *J. Phys. Chem.* **36**, 549 (1932).
- (7) KOLTHOFF, I. M., AND PEARSON, E. A.: *Ind. Eng. Chem., Anal. Ed.* **4**, 147 (1932).
- (7a) MOLTZAU, R., AND KOLTHOFF, I. M.: *J. Phys. Chem.* **40**, 637 (1936).
- (8) MOSER, L., AND BEHR, M.: *Z. anorg. allgem. Chem.* **134**, 49 (1924).

THE PHYSICAL CHEMISTRY OF FLOTATION. VIII

THE PROCESS OF ACTIVATION

ELSIE EVELYN WARK AND IAN WILLIAM WARK

Department of Chemistry, University of Melbourne, Melbourne, Australia

Received April 24, 1956

Potassium ethyl xanthate, which is not normally able to induce the flotation of sphalerite (ZnS), becomes effective in the presence of a low concentration of copper sulfate. This action of a copper salt, known technically as "activation," is used for the flotation of sphalerite following the flotation of galena by xanthate alone. It is generally assumed that the sphalerite becomes coated with a thin film of copper sulfide, which can adsorb the xanthate. In support of this interpretation, it is urged that many copper-bearing minerals do adsorb xanthate from very dilute solutions. It has been demonstrated by several methods that sphalerite acquires a coating of a copper-bearing film when it is immersed in a copper sulfate solution. This coating is not removed by a water washing, but is removed by treatment with a dilute solution of sodium cyanide (12). Three molecules of cyanide per atom of copper are sufficient to prevent the activation of the sphalerite by copper sulfate, presumably because a soluble cupricyanide is formed which greatly reduces the copper-ion concentration. The minimum concentration of copper ions required to activate sphalerite is of the order 10^{-28} (12).

Many lead-zinc ores contain sufficient soluble copper to activate the sphalerite and thus to interfere with its separation from galena. Addition of sodium cyanide during grinding and conditioning of the ore usually prevents flotation of much of the sphalerite with galena, but some operators think that cyanide does not completely prevent activation. If this be true, the activation must be due to some other ion, not removable from the sphalerite surface by cyanide. Lead salts would cause activation of this type but sodium carbonate, if present, would tend to precipitate them and thus to prevent activation. The results cited later may therefore be of more than academic interest.

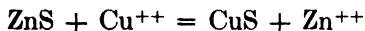
Berl and Schmidt (1), using a spectroscopic method to determine the amount of heavy metal ions removed by adsorption, have demonstrated that galena and sphalerite both adsorb copper and that sphalerite also adsorbs lead from solutions of their soluble salts. Ravitz and Wall (8), who used an iodometric method to measure the amount of copper removed

from a copper sulfate solution by sphalerite, claim that the adsorption is almost complete within a minute; that for particles of 50 microns and over, which is the size preferred in practice, the amount of copper sulfate required for maximum recovery in flotation is approximately equivalent to the amount that would be required for the formation of a unimolecular film, and that considerably greater amounts of copper up to a fixed maximum value can be adsorbed from concentrated solutions. They suggest that the maximum amount adsorbed is just sufficient to coat with a unimolecular film the surfaces of all the unit crystal blocks, whose size is set at 0.37 micron, penetration into the crystal lattice being assumed.

In some instances activation of a mineral can be effected by adding a salt of the metal of the mineral. Thus, when using methyl xanthate as collector, chalcopyrite can be activated by copper sulfate. Similarly, the addition of zinc sulfate helps in the flotation of sphalerite by amyl xanthate. This type of activation is connected with the mechanism of the adsorption of the xanthate, and has led us to the conception of an "adsorption solubility product."

Another type of activation, exemplified by the action of sodium sulfide on anglesite and cerussite, which has already been considered (14), will not be discussed here.

It has generally been assumed that activation of sphalerite by copper sulfate is due to the formation of a surface coating of cupric sulfide, formed, in accordance with the solubilities, by the action



If one accepts the evidence of Ravitz and Wall that a unimolecular film suffices for flotation¹, one would not expect such a film to possess the surface properties of massive covellite (CuS). Experiment does, in fact, indicate that the film has not the properties of massive covellite, at least with regard to depression by sodium cyanide or caustic soda. Figure 1, constructed from earlier papers (12, 13), shows for covellite and for pre-activated sphalerite the relationships between the concentrations of cyanide and the pH value necessary to prevent air-mineral contact in the presence of 25 mg. per liter of potassium ethyl xanthate. (By preactivation is meant immersion of the sphalerite specimen in a copper sulfate solution before it is placed in the xanthate solution.) Contact for either mineral is possible below or to the left but not above or to the right of its curve.

If copper sulfate is present as well as xanthate, a considerably higher concentration of cyanide is necessary to prevent contact. With 150 mg.

¹ One could not at the same time accept the suggestion of Taggart, del Giudice, and Ziehl (9) that this film must become oxidized before it can adsorb xanthate, for if it did we should have simply a unimolecular adsorbed film of copper sulfate on zinc sulfide.

of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 25 mg. of the xanthate per liter, the corresponding curve for sphalerite, also taken from an earlier paper (13), is shown in figure 2. A similar curve has been determined by Mr. A. B. Cox for stibnite which, like sphalerite, requires activation before it will respond to a neutral solution of ethyl xanthate. It will be seen that the curves for the two minerals are very similar. The corresponding curve for covellite in the presence of copper sulfate was not determined completely, but it lies very much higher than these two curves. It is apparent, therefore, that

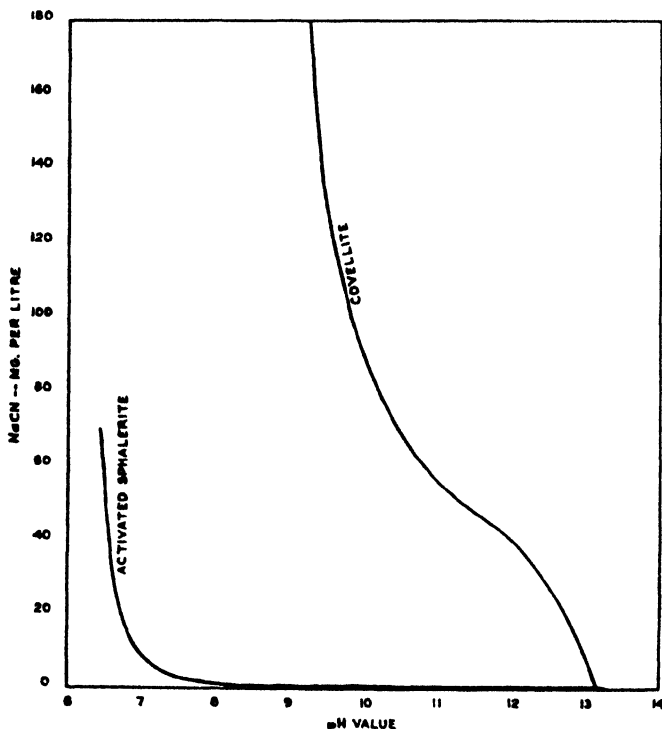


FIG. 1. Relationship between pH value and concentration of sodium cyanide necessary to prevent contact at surfaces of covellite and activated sphalerite. Potassium ethyl xanthate = 25 mg. per liter. No added copper sulfate.

when copper sulfate activates a sulfide mineral, the coating produced is not identical with covellite. Nor is it probable that the coatings for different minerals are held equally firmly: the non-identity of the activation curves for galena and sphalerite when using sodium diethyl dithiophosphate as a collector suggests that they are not (13).

For reasons which will be cited elsewhere we do not agree with the contention of Taggart, del Giudice, and Ziehl (9) that the possibility of adsorption of a collector is governed entirely by the solubilities of the metallic

salts of that collector. However, as these authors state, there is little evidence to show whether adsorption of an *activator* is governed entirely by solubility considerations. We set out, therefore, to determine which metallic salts are effective as activators for sphalerite. If solubilities alone are responsible, immersion of a sphalerite specimen in a solution of a salt of any metal whose sulfide is less soluble than sphalerite may cause activation, but immersion in a solution of a salt of a metal whose sulfide is more soluble than sphalerite should not. In testing this view we proposed to use ethyl xanthate to indicate whether adsorption of the metal ions

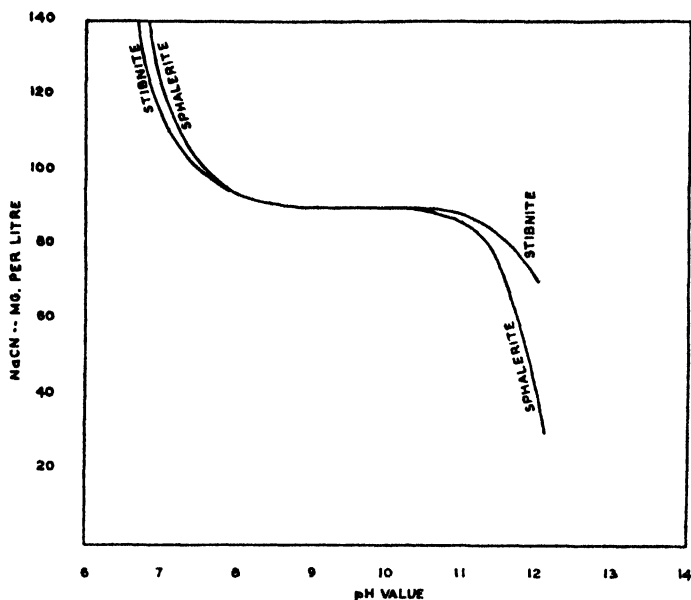
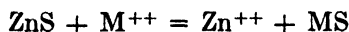


FIG. 2. Relationship between pH value and concentration of sodium cyanide necessary to prevent contact at surfaces of sphalerite and stibnite. Specimens pre-activated in a solution of copper sulfate. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ = 150 mg. per liter; potassium ethyl xanthate = 25 mg. per liter.

had occurred, the procedure being to immerse the pretreated sphalerite in a xanthate solution and to observe whether a bubble of air could effect contact with it. An assumption was made here, namely, that if the surface is filmed by the metal ions, it will respond to ethyl xanthate. When the tests were begun this seemed probable enough, for the heavy metal sulfide minerals that had been tested had all responded to ethyl xanthate. However, during the progress of the work it was found that stibnite (Sb_2S_3) does not respond to neutral ethyl xanthate solutions, but only to slightly acid solutions of ethyl xanthate. This raised doubts concerning the validity of our initial assumption. Consequently, if the treated sphalerite

specimen failed to respond to a neutral ethyl xanthate solution it was tested also in an ethyl xanthate solution at a pH value of between 4 and 5. More potent collectors could not be used, since they cause contact at a sphalerite surface in the absence of activators (13). Despite these precautions, the absence of a response to ethyl xanthate, though it suggests that adsorption of the metal ions has not taken place, does not prove it. On the other hand, if a response has been obtained, the conclusion is definite that activation has taken place.

Kolthoff (4) cites three values between 5×10^{-26} and 8×10^{-26} for the solubility product of α -zinc sulfide, and the single value 10^{-24} for β -zinc sulfide. Let us consider activation by the salt of a bivalent metal (M). If the process is dependent only upon solubilities, it follows that the filming process,



occurs if on the addition of the salt of M,

$$\frac{(\text{M}^{++})}{(\text{Zn}^{++})} > \frac{(\text{MS})}{(\text{ZnS})}, \text{ i.e., } > \frac{\text{Solubility product of MS}}{\text{Solubility product of ZnS}}$$

The concentration of zinc ions must be very small: we should therefore expect filming by any bivalent metal, the solubility product of whose sulfide is equal to or lower than the solubility product of zinc sulfide. For filming to occur under this mechanism it would be necessary that the term:

$$\frac{(\text{Solubility product of ZnS})}{(\text{Zn}^{++})} \text{ should be greater than}$$

- (i) $\frac{\text{Solubility product of MS}}{(\text{M}^{++})}$ for bivalent metal salts
- (ii) $\frac{\text{Solubility product of M}_2\text{S}}{(\text{M}^+)^2}$ for univalent metal salts
- (iii) $\frac{\text{Solubility product of (M}_2\text{S}_3)^{1/3}}{(\text{M}^{++})^{2/3}}$ for trivalent metal salts

Unfortunately, the solubility products of the metallic sulfides are not known with any degree of certainty. Table 1 sets out recorded values from various sources. Because of the decomposition of ferric sulfide it is doubtful whether the figures for it are significant. There is an enormous discrepancy between the figures cited in Landolt-Börnstein's tables for the solubilities and solubility products of heavy metal sulfides. Thus the solubility of mercuric sulfide, given as 1.2×10^{-6} , corresponds to a solubility product of the order 10^{-16} ; the recorded value is 10^{-53} . For lead sulfide the corresponding figures are 10^{-9} and 10^{-29} . Though greater care

TABLE 1
Solubility product of metal sulfides

METAL	KOLTHOFF (4)	LANDOLT-BÖRNSTEIN (5)	LATIMER AND HILDEBRAND (6)	HANDBOOK OF CHEMISTRY AND PHYSICS (3)	TREADWELL-HALL (10) (CALCULATED)
Barium.....				Decomposes	8×10^{-4}
Strontium.....				Decomposes	
Calcium.....				Decomposes	
Magnesium.....				Decomposes	
Beryllium.....				Decomposes	1.4×10^{-11}
Aluminum.....				Decomposes	
Chromium.....				Decomposes	
Uranium.....				Decomposes	
Cerium.....				Decomposes	1.1×10^{-15}
Titanium.....				Decomposes	
Manganese.....	7×10^{-16} to 6×10^{-22}	1.4×10^{-23}	10^{-15}	1.4×10^{-15}	
Ferrous.....	4×10^{-19} to 3×10^{-22}	2×10^{-19}	10^{-19}	3.7×10^{-19}	
Ferric.....					(8×10^{-23})
Zinc.....	10^{-24} to 5×10^{-28}				
Nickel.....	1.1×10^{-27}	10^{-21} to 10^{-26}	10^{-23}	1.2×10^{-23}	
Cobalt.....	1.9×10^{-27}	3×10^{-28}	10^{-24}	1.4×10^{-24}	
Thallium.....	7×10^{-23} to 10^{-24}	10^{-23}		3×10^{-28}	6×10^{-21}
Lead.....	3.4×10^{-28}	10^{-29}			
Cadmium ..	7×10^{-23} to 5×10^{-29}	4×10^{-29}	10^{-23}	3.4×10^{-23}	
Cuprous.....				3.6×10^{-29}	
Cupric.....	7×10^{-41} to 10^{-42}	8.5×10^{-45}	8×10^{-49}	2×10^{-47}	8.5×10^{-41}
Silver.....	(av.) 10^{-36}	1.6×10^{-49}	2×10^{-49}	8.5×10^{-45}	
Mercurous.....	10^{-47}			1.6×10^{-49}	
Mercuric.....	3×10^{-44}				
Bismuth.....	1.6×10^{-72} (?)	10^{-33}	1×10^{-33}	4×10^{-33} to 2×10^{-49}	4×10^{-54}

is usually taken in the determination of solubility products, the values recorded for them are of doubtful value, for the assumptions upon which the determinations are based cannot be justified. The greatest weight must be attached to Kolthoff's figures, which were obtained from a critical study of the work of earlier writers.

Even if it were proved that solubilities alone governed activation, it is evident that the solubilities of some of the sulfides are not known with sufficient accuracy for one to be able to predict whether zinc sulfide should be activated by solutions of the corresponding heavy metal salts. The results obtained in this investigation do not, therefore, enable one to decide whether activation of sphalerite should be attributed to simple double decomposition or to "exchange adsorption" (2). There is no doubt that salts of the metals that form the least soluble sulfides activate sphalerite, nor that salts of the metals that form the most soluble sulfides do not activate it. It has not been settled, however, whether activation is governed entirely by solubility considerations for salts of metals whose sulfides are of the same order of solubility as zinc sulfide.

EXPERIMENTAL

Method I: The sphalerite specimen was polished in the usual manner (11), placed in a 10 mg. per liter solution of the heavy metal salt, and after thirty minutes, 25 mg. per liter of potassium ethyl xanthate was added. After a second period of thirty minutes the specimen was tested with a captive bubble of air to ascertain whether it had acquired a xanthate film. If contact was possible between the bubble and the surface the angle of contact was measured at intervals up to two hours. The recorded values were measured two hours after the xanthate addition; usually a steady value was reached much sooner than this.

Method II: An alternative method of activation was tried for each metal, namely, to stand the specimen for thirty minutes in a 1 g. per liter solution of the salt, then after rinsing in water, to transfer to a 1 g. per liter xanthate solution. This method possesses the advantage that there is no precipitate of heavy metal xanthate in the solution to hinder contact with the surface.

Method III: For reasons already stated, if neither of these procedures proved that activation had occurred, a third was tried, namely to test the pretreated specimen in an acidified 200 mg. per liter ethyl xanthate solution at a pH value of between 4 and 5. Control tests showed that in the absence of activators contact with sphalerite was impossible under these conditions: in solutions containing 500 mg. of potassium ethyl xanthate per liter, weak and irregular contact is obtained if the pH value is reduced to 4 by addition of hydrochloric acid, and with very high xanthate concen-

trations and acidities an angle of contact only two or three degrees less than 60° is obtained. This contact is not due to products of the decomposition of the xanthate in acid solutions. Nor is it due to the iron that is almost invariably contained as an impurity in the sphalerite, for resin blende, marmatite (a solid solution of iron sulfide in zinc sulfide), and cleio-phane (an iron-free blende) all behave similarly. Curves obtained previously (13) suggest that sphalerite might respond, without activation, to high ethyl xanthate concentrations in acidified solutions.

Method IV: The contact tests were supplemented by direct flotation tests in stoppered cylinders. The procedure was similar to that adopted in methods I, II, and III, except that a suspension of sphalerite in water was used for the attempted activation; after additions of 20 mg. per liter of terpineol as frother, of xanthate as collector, and of acid, if there was no response in neutral solutions an attempt was made to float the mineral by shaking the stoppered tube vigorously.

PURITY OF CHEMICALS

Since even 1 mg. of copper sulfate per liter is an activator for sphalerite, it is essential that the compounds tested should be free from any substantial amounts of copper or other heavy metal salts. The purest specimens obtainable were recrystallized before use, and the xanthates were purified as described previously (11). Antimony trichloride was redistilled. Titanium trichloride was crystallized from the commercial 15 per cent solution by adding alcohol and ether, washing with ether, and then recrystallizing from alcohol by addition of ether. The water used was distilled from glass apparatus and was copper-free.

TECHNIQUE OF POLISHING

At one time during the investigation it became so difficult to obtain clean polished specimens that, had we not had several years' experience to convince us that clean specimens of sphalerite were not air-avid, we should have believed that they were. As some other investigators have apparently experienced similar difficulties, a description of the methods adopted to overcome them may not be out of place. Since one of us experienced greater difficulty than the other, and since trouble was encountered particularly in hot weather, it was suspected that the natural grease of the hands was responsible. Linen gloves lessened but did not completely eliminate the trouble, but surgical rubber gloves, when properly treated, did remove it. The gloves must be kept in such a condition that water readily wets them; this can be done by washing them with wet talc powder. Subsequently it was found that rubbing the hands with talc powder may suffice to remove the natural grease, and it is then possible to dispense with gloves.

TABLE 2
Activation of sphalerite by metallic salts

ELEMENT	SALT USED	ANGLE OF CONTACT			DIRECT FLOTATION TEST METHOD	
		Method I	Method II	Method III	Neutral solution	Acid solution
Barium.....	Nitrate	Nil	Nil	Nil	No flotation	No flotation
Strontium.....	Chloride	Nil	Nil	Nil	No flotation	No flotation
Calcium.....	Nitrate	Nil	Nil	Nil	No flotation	No flotation
Magnesium.....	Chloride	Nil	Nil	Nil	No flotation	No flotation
Beryllium.....	Nitrate	Nil	Nil		No flotation	No flotation
Aluminum.....	Potassium alum	Nil	Nil		No flotation	No flotation
Chromium.....	Potassium alum	Nil	Nil	Nil	No flotation	No flotation
Thorium.....	Nitrate	Nil	Nil		No flotation	No flotation
Uranium.....	Nitrate	Nil	Nil		No flotation	No flotation
Titanium.....	Trichloride	Nil	Irregular*	Irregular	No flotation	No flotation
Titanium.....	Double oxalate (K)	Nil	Irregular	Irregular	No flotation	No flotation
Manganese.....	Sulfate	Nil	Nil		No flotation	No flotation
Ferrous.....	Sulfate	Nil	Nil		No flotation	No flotation
Ferric.....	Ammonium alum	Nil	Nil		No flotation	No flotation
Stannous.....	Chloride	Nil	Nil*	Nil	No flotation	No flotation
Stannic.....	Double chloride (Na)	Nil	Nil	Nil	No flotation	No flotation
Arsenic.....	Trioxide	Nil	Nil	60°	No flotation	Good flotation
Antimony.....	Trichloride	Nil	Nil*	61°	No flotation	Good flotation
Nickel.....	Sulfate	Nil	Nil	Nil	No flotation	No flotation
Cobalt.....	Sulfate	Nil	Nil	61°	No flotation	Weak flotation
Thallium.....	Nitrate	Irregular	60		Fair flotation	Fair flotation
Cerium.....	Sulfate	Nil	60		Good flotation	Good flotation
Lead.....	Nitrate	61	62		Good flotation	Good flotation
Cadmium.....	Sulfate	61	59		Good flotation	Good flotation
Cupric.....	Sulfate	61	60		Good flotation	Good flotation
Silver.....	Nitrate	62	61		Good flotation	Good flotation
Mercuric.....	Chloride	63	60		Good flotation	Good flotation
Mercurous...	Sulfate	61†			Good flotation	Good flotation
Bismuth...	Nitrate		62*		Good flotation	Good flotation
Gold.....	Acid chloride		61		Good flotation	Good flotation
Platinum...	Chloroplatinic acid		Irregular	58	Fair flotation	Good flotation

* Less than 1 g. per liter because of hydrolysis.

† Saturated solution.

EXPERIMENTAL RESULTS

The results of the investigation are summarized in table 2. Except for titanium the results from direct flotation tests are in agreement with those from contact tests. The contact induced by some of the salts was not of the same order as that induced by copper sulfate, for example. When using copper sulfate as activator, the xanthate caused a rapid and complete response to an air bubble, but when using a titanium salt the reaction was slow and irregular; only on rare occasions was the characteristic angle (60°) obtained, and then only over a portion of the surface. In direct flotation tests, the presence of copper sulfate results in the formation of a highly mineralized froth that is stable for days and up to 75 per cent of the sphalerite can be floated. On the other hand, titanium salts, though they cause more sphalerite particles to reach the surface than would do so in their absence, do not result in the formation of a permanent mineralized froth. With thallium nitrate as activator, it seems at first that a stable froth will form, but although much of the mineral is carried to the surface by the bubbles, the froth does not persist, and most of the mineral falls. With cobalt sulfate the flotation is still less permanent.

Owing to hydrolysis, difficulties arose in testing salts of bismuth, tin, and antimony. Activation was attempted both in solutions acidified to prevent hydrolysis and in neutral suspensions containing the hydroxide. With bismuth, sufficient of the salt remains in solution at $\text{pH} = 7$ to activate sphalerite, and ethyl xanthate then induces the customary contact angle and leads to excellent flotation. With antimony trichloride, however, only in slightly acid solutions is there sufficient antimony for activation; the xanthate solution also is effective only in acid solutions. Neither in acid solution nor in neutral solution was stannous chloride an activator for sphalerite. Titanium trichloride also hydrolyzes, and it was the partly decomposed solution ($\text{pH} = 3.5$) that was in part effective as an activator. Arsenic trioxide dissolves very slowly in water; hydrochloric acid hastens the solution process and the excess acid can be neutralized before testing.

Sphalerite reduces chloroauric acid; a precipitate of metallic gold is formed on the surface of the sphalerite when using gold chloride. It is doubtful, therefore, if the activation should be attributed to the formation of a film of gold sulfide.

Cobalt and nickel are generally believed to form fairly insoluble sulfides. The failure of hydrogen sulfide to precipitate the metals from acidified solutions of their salts is difficult to understand, for the sulfides themselves do not dissolve in dilute acid. Middleton and Ward (7) have shown, however, that the mechanism of the precipitation is complex, and that precipitation of the true sulfides does not usually occur. Attempts to activate sphalerite by a solution of nickel sulfate, made alkaline by ammonia and stabilized by ammonium chloride, were not successful.

It is surprising that neither for stannous nor for stannic salts could con-

ditions be found that led to activation of sphalerite. We found, however, that stannic sulfide is not precipitated from a 1 g. per liter solution of the double chloride by sodium sulfide, despite the reported low solubility of stannic sulfide, 0.0002 g. per liter.

Some results for silver and mercury, cited in an earlier paper (11), seemed to indicate that if the heavy metal salt was in stoichiometric excess of the xanthate, activation was not obtained. This indication was not substantiated, for on varying the concentrations over a wider range, it was found that contact was sometimes possible with the metal salt in excess. Precipitates of the heavy metal xanthates are responsible for the difficulties, and if the surface is freed from them (by wiping with a clean linen pad) contact is possible whatever the relationship between the metal and xanthate additions. In all the tests now recorded the surfaces tested were treated in this manner to free them from precipitates, visible or invisible, that would hinder contact.

SUMMARY

1. It has been found that salts of the metals platinum, gold, bismuth, mercury, silver, copper, cadmium, lead, cerium, antimony, and arsenic "activate" sphalerite in a manner such that it responds to ethyl xanthate and floats readily. Thallium and cobalt induce a somewhat weaker response and titanium, though it does have a weak influence on the response of the mineral to an air bubble, is not a sufficiently powerful activator to cause flotation.

2. In general, the metals that are effective as activators form relatively insoluble sulfides and those that are not effective form relatively soluble sulfides.

3. It is not possible to decide whether solubility considerations alone govern the activation process. Thallium, whose sulfide is reputed to be more soluble than that of zinc, does activate sphalerite, and tin salts, which give less soluble sulfides, do not activate sphalerite. However, the reported solubility products are not to be relied upon.

One of us (E. E. W.) wishes to express her thanks to the University of Melbourne for a scholarship that has rendered the work possible. The other author wishes to acknowledge the help of the companies by which he is employed, viz., Broken Hill South Pty. Ltd., North Broken Hill Ltd., Mt. Lyell Mining & Railway Co., Zinc Corporation Ltd., Electrolytic Zinc Co. of Australasia Ltd., and the Burma Corporation Ltd. Our thanks are due also to Messrs. H. Hey and A. B. Cox for valuable help and advice.

REFERENCES

- (1) BERL AND SCHMIDT: *Kolloid-Z.* **65**, 264 (1933).
- (2) FREUNDLICH: (Hatfield's translation) *Colloid and Capillary Chemistry*, p. 204. London (1926).

- (3) Handbook of Chemistry and Physics, p. 845. Chemical Rubber Publishing Company, Cleveland (1934).
- (4) KOLTHOFF: J. Phys. Chem. **35**, 2716 (1931).
- (5) LANDOLT-BÖRNSTEIN: Physikalisch-chemische Tabellen, Vol. II, 5th edition, p. 1180. Springer, Berlin (1923).
- (6) LATIMER AND HILDEBRAND: Reference Book of Inorganic Chemistry, p. 389. The Macmillan Co., New York (1929).
- (7) MIDDLETON AND WARD: J. Chem. Soc. **1935**, 1459.
- (8) RAVITZ AND WALL: J. Phys. Chem. **38**, 13 (1934).
- (9) TAGGART, DEL GIUDICE, AND ZIEHL: Trans. Am. Inst. Mining Met. Engrs. **112**, 348 (1934).
- (10) TREADWELL-HALL: Analytical Chemistry, Vol. 1, p. 458. London (1932).
- (11) WARK AND COX: Trans. Am. Inst. Mining Met. Engrs. **112**, 189 (1934).
- (12) WARK AND COX: Trans. Am. Inst. Mining Met. Engrs. **112**, 245 (1934).
- (13) WARK AND COX: Trans. Am. Inst. Mining Met. Engrs. **112**, 267 (1934).
- (14) WARK AND COX: Am. Inst. Mining Met. Engrs., Tech. Pub. 659 (1936).

THE RELATIONSHIP BETWEEN CONDITIONS GOVERNING RUPTURE AND FLOW IN FLOUR DOUGHS

P. HALTON¹

Research Association of British Flour Millers, St. Albans, England

AND

G. W. SCOTT BLAIR

Physics Department, Rothamsted Experimental Station, Harpenden, England

Received April 8, 1936

INTRODUCTION

In an earlier paper (6) it was shown that there is a general correlation between the bread-making qualities of flour doughs and certain of their physical properties, chiefly relaxation time (viscosity/shear modulus) and the rate of fall of viscosity during fermentation. The importance of a further dough property, the tendency to tear when stretched, was also realized, but the discussion of the significance of this in terms of viscosity, modulus, etc., was left until further experiments had been completed. The tendency to tear varies from dough to dough, but only becomes apparent to the baker when it reaches the stage when the dough "tears" easily under bake-house manipulation. Such doughs are called "short" and the baker speaks of varying degrees of "shortness," such as "slight shortness" or "extreme shortness." Before this stage is reached, however, the baker does not recognize this tendency to tear, although it is there and probably influences the bread-making quality of the dough. It may, for example, be an important factor in determining whether a dough bakes into a loaf having the fine vesiculated crumb generally associated with an all-Manitoba flour or the coarse and open crum from an all-English flour.

A direct measure of the tensile strength of a flour dough is at the moment impossible, partly because the value obtained depends so greatly on the conditions of stress application, and partly because the excessive flow and consequent thinning of the test piece before rupture makes a determination of the cross section impossible.

The conception of "shortness" as determined by the baker is a complex one, and probably depends partly on ductility as well as on tensile strength. Ductility represents the critical deformation of the material at the point

¹ By mutual agreement the authors' names are given in alphabetical order and no seniority is implied.

of rupture, the tensile strength being the critical stress. The relationship between the two is complex, and it is sufficient for the present purpose to point out that ductility is a function of viscosity, shear modulus, and elastic after-effect as well as of tensile strength. When a piece of dough is extended,² since the stress built up in the dough is proportional to the viscosity and to the rate of extension, the tensile strength will be exceeded after quite a small elongation if the extension is rapid, whereas a slow pull will allow a big deformation before rupture occurs. Thus for a direct test carefully controlled conditions are essential, whereas the baker judges shortness partly by extending the dough at quite uncontrollable rates and stresses, and partly by observing the stretching and tearing of a mass of dough under its own weight. Shortness is therefore not a very sharply defined property, and only comparatively wide differences can be reliably observed. Such wide differences do, however, occur even within the range of commercial flours, and some quantitative measure of them is essential for a further understanding of the nature of shortness. Measurements of ductility at unknown stress but controlled rates of deformation, although fairly reproducible, do not correlate with "shortness" as determined by handling. It has been shown (15) that the size of a bubble which can be blown in a dough is only a measure of "shortness" for doughs in which this property is predominant. In more extensible doughs, the shear modulus plays an important part in determining extensibility (*vide infra*).

Although the relationships between rupture and flow conditions are not yet fully understood, certain phenomena have been observed which indicate a method by which shortness may be measured. This method depends on the relationship between the rate at which viscosity falls with increasing stress (structural viscosity)³ and the brittleness of materials (13). If a dough were a true highly viscous fluid, it would extend until the test piece narrowed to a thread before rupture; if it were a solid, up to a limiting stress (tensile strength) it would hardly deform at all (viscosity infinite) and at this stress it would break right across. This suggests that the more a dough approximates to a true fluid, the less "short" it is likely to be.

A certain correlation between high work-hardening and shortness had been observed in the rheogram experiments,⁴ and it has been known for some time that high work-hardening is generally associated with big structural viscosity, but owing to the very limited range of stress available in the rheogram method, the full implications of this were not realized, although the significance of the distribution of relaxation times in determining plastic properties had already been appreciated (14).

² It is here assumed that the elastic extension is small in comparison with the non-recoverable extension.

³ The use of this term is convenient, but does not imply agreement with the theoretical treatment of the Ostwald school.

⁴ For a description of the rheogram method see references 6 and 12.

If a dough is extended until it breaks, a fibrous structure⁵ can be observed with the naked eye, especially clearly in the case of a short dough. Rupture occurs as a result of the tearing apart of the fibers; the more coarse the fiber structure, the sooner the mass disintegrates, because the tearing of a single fiber makes a big rent and greatly decreases the area over which the load is distributed. Local rupture results, as Griffith (5) has emphasized, in a big conversion of potential into kinetic energy, producing a local fall in viscosity. Griffith claims that in the case of metals this effect is responsible for the fact that measured tensile strengths are always so much smaller than the theoretical ones.

The formation of gross fibers in the dough as it is deformed not only causes an increase in viscosity and shear modulus (work-hardening) but also, by producing a heterogeneity of structure, effects a progressive slipping of fibers as stress increases, which shows itself in high structural viscosity. The shear angle gets more and more distorted the grosser the fibers become. Tammann and Rejtö (*vide* Goubkin (4) consider that work-hardening in metals may be ascribed entirely to this effect, and Nádaï (7) states that it is responsible for brittleness, although it is now claimed (3) that this is an exaggeration.

When the junction between two fibers slips and breaks, a rent is formed and these previously extended fibers contract, making the rent worse. It is clear that the extent of widening of the rent will depend on how much the elastic elements were extended prior to rupture. The modulus of the fibers thus affects the conditions of rupture, and in comparing the structural viscosities of doughs it is best to adjust their moisture contents such that comparisons can be made at a fixed modulus (6). It must be remembered that whereas the measurable viscosity of a heterogeneous material is probably a function of the viscosities of all its parts at the stress in question, the tensile strength depends on the resistance of the weakest part. If there is a wide distribution of viscosities amongst the elements making up the dough, this will result both in a high structural viscosity and in a tensile strength which is low for the mean viscosity. Heterogeneity, reflecting a high structural viscosity, thus always tends to favor rupture and homogeneity favors flow.

The nature of the process of fiber formation in dough is very little understood, nor is it known why some flours give doughs which are abnormally prone to it, though it would be surprising if there were no natural variation in this, such as is found in all other physical properties.

Potel (8) and Potel and Chaminade (9) have shown that mild oxidation increases shortness in dough, while reduction diminishes it. The processes may be followed by observing changes in oxidation-reduction potential.

⁵ The term "fibrous structure" really implies no more than the existence of mechanical anisotropy, but is conveniently used in this sense even in describing properties of crystals (11).

In view of the recent work of Astbury, Dickinson, and Bailey (2) one might suggest that oxidation effects some type of mild denaturation involving "the liberation or generation of peptide chains which aggregate on coagulation into parallel bundles like those found in the structure of β -keratin and similar fibres." In the case of dough, these fibers only manifest themselves when the dough is extended. Whether the process is actually reversible on subsequent reduction, or whether the reducing agent acts at different spots in the dough structure is not known.

The fiber structure of dough is also enhanced by the addition of many other materials such as the fats, which, by modifying the viscosity at certain points in the dough, tend to increase heterogeneity, and hence structural viscosity.

Astbury (1) has pointed out that the amino acid⁶ cystine ($\text{HOOC} \cdot \text{CH}(\text{NH}_2)\text{CH}_2\text{S} \cdot \text{SCH}_2\text{CH}(\text{NH}_2) \cdot \text{COOH}$) can form strong cross linkages between protein chains, like the rungs in a ladder. It has been found that cystine does make unyeasted dough feel less short. Cysteine ($\text{HOOC} \cdot \text{CH}(\text{NH}_2)\text{CH}_2\text{SH}$) would be expected to be less effective in this respect, because only one end of the molecule can attach itself to the protein chain, but on the other hand, it is a reducing agent, which may account for the fact that in practice it is found to be not much less effective than cystine. Other amino acids, such as aspartic acid and *m*-aminobenzoic acid, become less effective as their polar properties diminish.⁷

The connection between structural viscosity and shortness has a profound influence on the interpretation of viscosity and modulus data in terms of baking values. The extent of elastic recovery (spring) of a short dough, as estimated at the high stresses used in handling, will not bear a normal relation to that determined at low stresses intended to correspond to those obtaining in the fermenting dough. Good spring has been shown to depend on high viscosity and low modulus, and since the latter does not alter very drastically with stress, a dough whose viscosity falls to any abnormal degree as stress is increased will also appear progressively to deteriorate in spring. This has been amply verified in the baker's experience. This means that in order to compare relaxation times (viscosity/modulus) with bakehouse data, the stresses at which they are determined should correspond with the internal stress built up in the dough during fermentation. The latter cannot yet be measured directly. This diffi-

⁶ Amino acids are found as products of proteolysis in the fermentation of flour dough, and in view of the above experiments it is tempting to suggest that changes in physical properties during fermentation may be ascribed to them. This is unlikely, however, since it has been shown (6) that these physical changes are only slightly affected by the presence of normal quantities of yeast, and Samuel (10) has demonstrated that in yeasted doughs the amino acids produced by fermentation are used up by the yeast in its metabolism (*vide infra*).

⁷ Some of these experiments were suggested to us by M. Potel.

culty has not been fully overcome, but it really means that both spring as measured by relaxation time and shortness as measured by structural viscosity in the test described below, have to be taken into account in assessing the quality of a flour. The extent to which these two properties are present in a dough determines its quality, but their relationship to each other, and how this varies in different flours, is not yet fully understood.

The experiments described below are designed to test whether the effect of various materials on the shortness of doughs as judged qualitatively by handling, can be shown to be paralleled by quantitative measurements of structural viscosity. If this can be done, although shortness is realized to be an extremely complex property, we shall be in a position to say that at least big differences in shortness can be measured by means of structural viscosity. In the later part of this paper, the question of smaller differences is discussed.

EXPERIMENTAL

Dough cylinders for viscosity measurements⁸ are prepared by extruding the dough through a metal "gun" at high pressure. It was noticed that when doughs showed about the same viscosity at the standard shearing stress of the order of 500 dynes per square centimeter the "shorter" doughs always came out of the gun faster and thus evidently had lower viscosities than the non-short doughs under the very high stress applied in the gun. To test this quantitatively, a flour was made short by the addition of different quantities of lard, and the viscosity (η) at 500 dynes per square centimeter under set conditions, together with the time (T) taken for a certain quantity of dough to be extruded from the "gun" under a load of 7 lb., were determined. The results, which are included in table 1, clearly indicate that over a big range of stress increasing shortness is accompanied by a rapidly increasing structural viscosity.

The time of extrusion from a gun is not a very satisfactory way of measuring viscosity, and it was of interest to determine whether the ratios of viscosities at two different stresses which could be applied in the standard technique would indicate big differences in shortness. The viscosities of a dough made without shortening agents were measured at 250 and 600 dynes per square centimeter, respectively, the ratio of these viscosities being 1.29. A similar test on a dough in which 2 per cent of lard had been incorporated showed a ratio of 1.54, 5 per cent of lard gave a ratio of 2.23, and 10 per cent of lard 2.25, although in the last case the stresses employed were no longer suitable. The structural viscosity had evidently been progressively increased by the shortening.

A test was then arranged in which other materials which were known to

⁸ The technique for measuring viscosity and modulus is described in the earlier paper (6).

affect shortness were added to flour when making doughs, varying quantities being used. The viscosity (η) and the modulus (n) at 500 dynes per square centimeter and the time of flow (T) out of the gun were measured under standard arbitrary conditions and compared in each case with a separate control. (This was done because temperature varied somewhat between the different experiments.) The results are given in table 1. η/T is taken as a measure of structural viscosity. It is clear that the effects, although perhaps not very accurately determined, are in entire

TABLE 1

Effect of certain substances on the viscosity, modulus, and structural viscosity of flour doughs

SUBSTANCE		DOSE IN PARTS PER MILLION OF FLOUR	$\eta/\eta_{\text{control}}$	n/n_{control}	T/T_{control}	$\eta/T/(\eta/T)_{\text{control}}$
decrease shortness	Cystine	4	0.86	1.07	0.89	0.96
		20	0.79	0.88	0.98?	0.80
		1,000	0.31	0.63	0.88	0.35
		2,000	Very low	Very low	0.82	Very low
	Cysteine	4	0.86	0.99	0.82	1.05
		20	0.71	0.77	0.73	0.98
		1,000	Very low	Very low	0.13	Very low
	Aspartic acid	500	0.59	0.85	0.91	0.65
		2,000	0.36	0.52	0.65	0.57
	<i>m</i> -Aminoben- zoic acid	500	0.61?	0.82?	0.85	0.72?
		2,000	0.64	0.76	0.77	0.84
increase shortness	Lard	40,000	0.97	1.25	0.63	1.53
		100,000	1.61	1.85	0.38	4.22
		200,000	1.48	3.10	0.10	14.8
	FeCl_3	High?	5.75	2.98	0.49	11.8
	HPO_3	8,000	1.71	0.93	0.40	4.3

agreement with the earlier findings, thus justifying the conclusion that for the range of variation considered the structural viscosity test gives a valid measure of shortness.

The treated and untreated doughs were compared at the same moisture contents. The addition of amino acids decreased the viscosity, modulus, and structural viscosity and in this way rendered the dough both softer and less short. The addition of extra water to a dough also lowers η , n , and η/T , and to compare the relative effects of cystine and water on struc-

tural viscosity it is necessary to make measurements at an arbitrarily chosen condition of consistency, such as a constant modulus.

A further experiment was therefore made in which doughs, with and without cystine, were compared at a modulus of 1.0×10^4 dynes per square centimeter. For the control dough $\eta = 0.85 \times 10^6$ dynes per second per square centimeter, $T = 40$ sec., and hence $\eta/T = 2.1 \times 10^4$. For the dough containing 5 parts of cystine per 100 parts of flour $\eta = 0.79 \times 10^6$, $T = 46$, and hence $\eta/T = 1.7 \times 10^4$.

Similar measurements were made at other moduli, and in each case the dough containing cystine had a slightly lower structural viscosity than the control dough. Thus a series of doughs of increasing water content and having the same moduli as the cystine doughs in table 1 would, dough for dough, have higher structural viscosities than the latter. Cystine thus makes dough less short partly by rendering it softer, as does water, and also by reducing the structural viscosity for a given consistency. To pro-

TABLE 2
Structural viscosity of doughs from some English flours

FLOUR NO	T	η	η/T
893	54	0.6×10^6	1.1×10^4
898	45	0.7×10^6	1.5×10^4
903	38	0.6×10^6	1.6×10^4
902	40	0.65×10^6	1.6×10^4
911	35	0.6×10^6	1.7×10^4
892	43	0.8×10^6	1.9×10^4
899	32	0.7×10^6	2.2×10^4
904	21	0.55×10^6	2.6×10^4

duce similar effects on consistency much larger quantities of water than of cystine are necessary. Although water and amino acids diminish shortness in a somewhat analogous way, namely through their effect on viscosity, the mechanism must be entirely different. Some tentative suggestions about the amino acid mechanism have already been discussed.

In addition to the above tests on flours whose degree of shortness had been artificially altered, a number of flours, all milled from English wheat and which when tested in the bakehouse had shown varying degrees of natural shortness, have also been examined.

These flours were tested under carefully controlled conditions in a constant-temperature room⁹ at 80°F., the temperature at which the flours had been examined in the bakehouse.

Doughs were made from each, and at intervals samples were taken on

⁹ This constant-temperature room was not available for the earlier experiments quoted in table 1.

which the values of T , η , and n were obtained. Curves were then drawn relating T , η , and n to the age of the dough, and from these, values of T and η corresponding to a modulus of 1.0×10^4 were obtained for each flour. These values, together with the ratio of η to T , are given in table 2.

Of these flours, which are arranged in table 2 in order of increasing η/T , the first two, Nos. 893 and 898, did not, according to the baker, show any signs of shortness. On the other hand, the last three, Nos. 892, 899, and 904, were all stated to be decidedly short. Of the three intermediate flours, Nos. 903 and 902 were rather short, while No. 911 was not short.

The correlation between η/T and shortness is therefore not perfect, and this may be due to one or more of the following reasons:

- (1) The impossibility of differentiating by feel any but comparatively large differences in shortness.
- (2) Shortness, while being mainly determined by structural viscosity and to a less extent by elastic modulus, may also be influenced by other factors which are not apparent at the moment.
- (3) The shortness of a test piece of dough from which the gas has been expelled may not be the same as that of the inflated parent dough which is examined by the baker. Shortness is more easily detected by feel in an inflated dough and is possibly influenced by the vesiculated structure of the inflated dough.
- (4) While T gives a rough measure of viscosity, the value obtained may be so influenced by other factors that η/T may give only an approximate value of structural viscosity.
- (5) Both η and T are not constants but are dependent on the stresses used in their determination. These stresses should approximate to those operating in the dough if exact correlation with bake-house experience is to be expected. The correct values for these stresses will only be found after considerable experience. In this connection it may be mentioned that the viscosities of the flours in table 2 were measured both at 600 and 200 dynes per square centimeter, but that the values of structural viscosities, as given by the ratio η_{200}/η_{600} , were so similar as to fail to differentiate one flour from another.

While therefore it is realized that the present methods of measuring structural viscosity and assessing shortness by feel are too imperfect to expect a close correlation between them in the case of the comparatively small differences between natural flours, there is little doubt that the two are intimately connected.

SUMMARY

1. It has been shown that the shortness (i.e., ease of tearing) of flour doughs is closely paralleled by the rate at which viscosity falls with increas-

ing stress (structural viscosity). A perfect correlation is not obtained, partly because neither property can be determined with great accuracy.

2. The effect on structural viscosity of certain substances (fats, amino acids, etc.) known to alter the shortness of dough has been measured, and the nature of the processes involved discussed.

3. The structural viscosities of doughs made from a batch of English flours have been determined, and it is found that the data are paralleled by fairly large differences in shortness as observed in the bakehouse.

4. The significance of shortness in terms of heterogeneity of dough, and its relation to tensile strength and ductility are tentatively discussed.

The authors wish to acknowledge their indebtedness to Dr. E. A. Fisher, Director of the Research Association of British Flour Millers, for his help and criticism in the writing of this paper.

REFERENCES

- (1) ASTBURY, W. T.: *Fundamentals of Fibre Structure*, p. 154. Oxford University Press (1933).
- (2) ASTBURY, W. T., DICKINSON, S., AND BAILEY, K.: *Biochem. J.* **29**, 2351 (1935).
- (3) BURGERS, W. G., AND BURGERS, J. M.: *First Report on Viscosity and Plasticity*, p. 188. Amsterdam (1935), Dutch Royal Acad. Sci.
- (4) GOUBKIN, S. I.: *J. Rheology* **3**, 501 (1932).
- (5) GRIFFITH, A. A.: *Proc. 1st Intern. Cong. App. Mech.*, p. 55 (1924).
- (6) HALTON, P., AND SCOTT BLAIR, G. W.: *J. Phys. Chem.* **40**, 561 (1936).
- (7) NÁDAI, A.: *Plasticity*. McGraw-Hill Book Co., New York (1931).
- (8) POTEL, P.: *Compt. rend. acad. agr. France* **21**, 115 (1935); *Ann. agron.* **5**, 691 (1935).
- (9) POTEL, P., AND CHAMINADE, R.: *Compt. rend.* **200**, 2215 (1935).
- (10) SAMUEL, L. W.: *Biochem. J.* **28**, 273 (1934); **29**, 2331 (1935).
- (11) SCHMID, E., AND BOAS, W.: *Krystallplastizität*. J. Springer, Berlin (1935).
- (12) SCHOFIELD, R. K., AND SCOTT BLAIR, G. W.: *Proc. Roy. Soc. London* **138A**, 707 (1932); **139A**, 557 (1933); **141A**, 72 (1933).
- (13) SCHOFIELD, R. K., AND SCOTT BLAIR, G. W.: *Nature* **136**, 147 (1935).
- (14) SCOTT BLAIR, G. W.: *Physics* **4**, 113 (1933).
- (15) SCOTT BLAIR, G. W., AND POTEL, P.: 1936. In process of publication, probably in *Bulletin des anciens élèves de l'école de meunerie*.

SOAPS: ELECTRIC CHARGE EFFECTS AND DISPERSING ACTION

W. M. URBAIN AND L. B. JENSEN

Swift & Company, Chicago, Illinois

Received April 24, 1936

INTRODUCTION

When a soap acts as a detergent, it functions in a number of ways. Two of its most important functions are its action as an emulsifying agent and as a deflocculating agent. By emulsification, soap suspends oily materials; by deflocculation, it suspends "inert" materials. Essentially both processes are the same in effect, for each results in the dispersion of the foreign material in the soap solution in such fashion that it can be removed with the soap solution or rinse water. While oily material is suspended almost entirely by emulsification, some solvent action by the soap solution on oils undoubtedly occurs (11, 13). However, in the relatively dilute solutions used in most washing operations, the solvent powers of soap solutions are small.

The purpose of this investigation was to consider the mechanism whereby soaps render emulsions of oily materials and suspensions of "inert" materials relatively stable. In this way it was thought possible to arrive at a more complete picture of the detergent action of soap.

THEORETICAL

In the case of oily materials emulsified by soap solutions in a washing operation, it is doubtful that water-in-oil emulsions are ever formed; only oil-in-water emulsions result. Ellis (3) and Powis (12) have shown that the stability of oil-in-water emulsions is dependent upon the value of the electric charge carried by the oil droplets. The higher the value of the charge, the more stable is the emulsion.

The oil droplets of an oil-in-water emulsion usually carry a negative charge. Since the hydrocarbon tail of the fatty-acid ion of a soap resembles the molecules of an oily material, the two should be more or less mutually soluble. If an oil droplet acquires the negative ion of a soap by dissolving this hydrocarbon tail, it also acquires the charge carried by the ion. In this way the negative charge of the oil droplet may be built up, and hence the stability of the emulsion increased.

In the case of the "inert" materials, it seems probable that a similar phenomenon would occur. Most particles, when suspended in water, assume a potential negative to that of water. The adsorption of a negative ion by such a particle serves to increase the negative potential. The magnitude of this effect on the potential increases with the valence of the ion adsorbed. For instance, the ferrocyanide ion increases the negative potential of graphite more than does the chloride ion (1).

McBain and his coworkers (8) have explained the anomalous conductivity of soap solutions by assuming the formation of colloidal micelles bearing a high electric charge-density. The formation of these micelles involves the fatty-acid ions of the soaps, and the micelles bear a negative charge. This high charge-density is analogous to a high negative valence. In view of the valence effect of ions on the electric potential, referred to above, it seems probable that, owing to the adsorption of these highly charged micelles, a soap should have a large effect on the potential of particles of inert materials suspended in a solution of the soap.

TABLE 1
Fatty acids used in the preparation of soaps

ACID	EASTMAN CATALOG NO.	MELTING POINT	SAPONIFI- CATION NUMBER	IODINE NUMBER
Caprylic.....	665			
Lauric.....			272.7	
Myristic.....	1116	53.8		
Palmitic.....	1213	61.9		
Stearic.....	402	68.5	196.3	0.54
Oleic.....		7.1	197.5	92.9

The effect of soap solutions on the charge of both the oil droplets of an emulsion and the particles of a suspension of an inert material can be determined by measurement of the zeta potential in an electrophoresis cell. This has been done in this investigation, and the results are reported below. An attempt has also been made to correlate the stability of the suspension of an inert material in soap solutions with the value of the zeta potential.

MATERIALS

Table 1 lists certain fatty acids from which the sodium and potassium salts were prepared according to the method of Ferguson and Richardson (4). It also includes the available constants and information as to sources of the acids.

Two oils were investigated, one a paraffin oil and the other a cottonseed oil. Neither oil contained more than 0.03 per cent free fatty acid calculated as oleic acid.

The inert material used in the majority of the electrophoresis experiments was a bleaching carbon Nuchar GL, made by the Industrial Chemical Sales Company of Chicago. It contained 1.85 per cent water-soluble ash and was grease-free. This carbon was screened to remove particles larger than 1 mm. in diameter.

APPARATUS

The electrophoresis apparatus was of the Northrop-Kunitz (9) type, and was obtained from the Arthur H. Thomas Company of Philadelphia, Pa. In order to work at elevated temperatures, a jacket was built around the apparatus and the desired temperature maintained by a thermostat and electric heater. Extensions were attached to the stopcock handles so that they could be manipulated from outside the jacket.

A potentiometer, used in conjunction with an assembly similar to that suggested by Gibbard (5), was employed to measure the potential drop across the electrophoresis cell.

EXPERIMENTAL PROCEDURE

The solutions were prepared directly from weighed amounts of the dry salts, including soaps, and freshly boiled distilled water which had not been allowed to cool. The solutions were brought directly to the desired temperature.

In order to prepare the emulsions, 1 cc. of the oil was shaken with 100 cc. of the water or solution. The excess oil was removed before the emulsion was used. To prepare the suspensions of inert materials, 0.1 g. of the solid was shaken with 100 g. of the solution.

When the electrophoretic velocity was to be determined, the suspension or emulsion was placed immediately in the electrophoresis cell, the velocity of the particles or globules determined with a stopwatch in the usual manner, and the potential drop across the cell measured. The microscope was focused at the level given by the equation

$$x = d \left(1/2 - \frac{1}{2\sqrt{3}} \right) \quad (1)$$

where d is the depth of the cell and x is the lower stationary level (a level at which the velocity of the liquid is zero).¹ Measurements of velocities were made only on particles from 1 to 3 micra in diameter and only on oil droplets of about 3 micra in diameter. Particles and globules of these sizes could be easily chosen in the microscopic field. The formation of a gel in the electrophoresis cell was found to cause mechanical disturbances

¹ The cell employed in this investigation was 0.940 mm. deep, and, following the above formula, the microscope was focused 0.198 mm. up from the bottom of the cell.

which interfered with the motion of the particles. Measurement of the velocity at 60° or 75°C. avoided this difficulty. At these temperatures, none of the solutions investigated formed gels.

When the actual stability of the suspensions formed was to be determined, the solutions containing the dispersed carbon were placed in 4-oz., oil-sample bottles, stoppered, and allowed to stand sixteen hours in an air thermostat at approximately 60°C. At the end of this period, the relative stability of the suspensions could be determined by visual inspection. The maintenance of a temperature of 60°C. prevented the formation of a gel by the soaps.

All pH measurements were made with a glass electrode.

CALCULATIONS

The electrokinetic potential can be calculated from the electrophoretic velocity by the equation

$$\zeta = \frac{4\pi}{D} \cdot \eta \cdot \frac{(V)}{(X)} \quad (2)$$

in which ζ is the electrokinetic potential, η the viscosity of the medium, V the velocity of the particle, X the potential gradient, and D the dielectric constant of the medium. All units are c.g.s.e. units.

Burton (2) has shown that, in the case of a silver sol, variation of the viscosity by changing the temperature produces a corresponding change in the velocities of the particles so that the product $\eta \frac{(V)}{(X)}$ is a constant. Gilford (6) has shown that, for a number of substances, temperature variation of the electrophoretic velocity depends only on the change of viscosity of the liquid phase. If the product $\eta \frac{(V)}{(X)}$ is constant, then the product ζD is also constant. Since D varies with the temperature, zeta must also vary. Hence, the value of zeta may be calculated from equation 2 for any temperature at which D is known.

The potentials (in millivolts) reported below are calculated to 25°C. The value of D at 25°C. was taken to be 78.5 (14). Although a comparison is made between these potentials at 25°C. and the stability of the suspensions obtained at 60°C., no discrepancy is introduced. Calculation of the potentials to 60°C. instead of 25°C. would shift all values by the same percentage, so that the relative order would remain the same; in this comparison only the relative order is considered.

Besides the potentials calculated from equation 2, the velocities actually observed, and from which the potentials were calculated, are listed. Since the velocities were obtained at various temperatures, these data cannot be compared with one another. The velocities are reported in micra per second per unit potential gradient.

RESULTS

The effect of sodium oleate on the zeta potentials of the oil droplets of two emulsions, one of a paraffin oil and the other of a refined cottonseed oil, was determined. Table 2 lists the results. The oil droplets bore an initial negative charge; this was increased by the presence of sodium oleate in the aqueous phase.

In the light of the work of Ellis (3), Powis (12), and others, these results indicate that the stabilization of oil-in-water emulsions by soap is due to the ability of soap to increase the negative charge of the oil droplets. Powis has shown that an emulsion is relatively stable if the oil/water

TABLE 2

Effect of sodium oleate on zeta potential of oil droplets of two oil-in-water emulsions

OIL PHASE	AQUEOUS PHASE	VELOCITY AT 28°C	ZETA POTENTIAL
		$\mu/\text{sec} / \text{volt/cm.}$	millivolts
Paraffin oil	Water only	7 1	-86
Paraffin oil.	0.0036 <i>M</i> sodium oleate	12 5	-151
Cottonseed oil	Water only	6 1	-74
Cottonseed oil	0.0036 <i>M</i> sodium oleate	11 6	-140

TABLE 3

Effect of a soap solution on zeta potential of different materials

MATERIAL	WATER		SOAP SOLUTION	
	Velocity at 28°C	Zeta potential	Velocity at 28°C	Zeta potential
	$\mu/\text{sec.} / \text{volt/cm.}$	millivolts	$\mu/\text{sec.} / \text{volt/cm.}$	millivolts
A carbon black	4 5	-60	5 3	-71
A water-insoluble dye	4 6	-62	5 9	-79
Ferric oxide	2 1	-28	5 8	-78
A strain of staphylococci bacteria	2 8	-34	4 1	-49

potential difference is greater than a definite critical value of approximately 30 millivolts (plus or minus). If the potential falls below this critical value, the emulsion breaks. The extraordinarily high values of the zeta potential obtained with the emulsions made with sodium oleate listed in table 2 indicate that these emulsions are very stable. This result is in agreement with the exceptionally good emulsifying powers of soaps.

It was next desired to determine the general effect of soaps on the charge of various inert particles. Table 3 lists the velocities and potentials observed for a number of different materials, first in distilled water and then in a dilute solution of a commercial soap. All these materials showed an increase in the negative zeta potential of the particles when placed in the

soap solutions over that observed in water. The data of table 3 indicate, therefore, that these particles adsorb the negative constituents of the soap.

The remainder of the study was continued with a single material, the bleaching carbon described under "Materials". While it is known that the value of the zeta potential depends upon the history of the carbon (10), nevertheless a single carbon can be used to determine the relative effect of

TABLE 4

Effect of concentration of soaps on zeta potential of carbon particles

(a) Sodium oleate at 23°C.

(b) Sodium palmitate at 60°C.

CONCENTRATION	VELOCITY	ZETA POTENTIAL	CONCENTRATION	VELOCITY	ZETA POTENTIAL
<i>moles per liter</i>	<i>μ/sec./volt/cm.</i>	<i>millivolts</i>	<i>moles per liter</i>	<i>μ/sec./volt/cm.</i>	<i>millivolts</i>
0.0007	6.5	-78	0.0007	10.7	-73
0.0013	6.6	-80	0.0014	11.0	-74
0.0023	6.7	-81	0.0021	10.7	-73
0.0026	6.9	-83	0.0036	10.2	-69
0.0033	7.3	-88	0.0054	12.0	-81
0.0039	7.4	-89	0.0072	11.0	-74
0.0049	7.4	-89	0.0107	11.2	-76
0.0056	7.2	-87			
0.0066	6.9	-83			
0.0082	6.6	-80			
0.0099	6.8	-82			

TABLE 5

Effect of various salts on zeta potential of carbon particles

COMPOUND, 0.0036 M	VELOCITY AT 23°C.	ZETA POTENTIAL
	<i>μ/sec./volt/cm.</i>	<i>millivolts</i>
Water.....	4.3	-52
Sodium acetate.....		-41*
Sodium sulfate.....	4.7	-57
Trisodium phosphate.....	5.2	-63
Potassium ferrocyanide.....	5.0	-60
Sodium oleate.....	6.9	-83

* From velocity measurement at 75°C.

different salts on the potential. This was done in order to obtain the data reported below.

Table 4 lists the data showing the effect of concentration of two different soaps on the electrophoretic velocity and zeta potential of the carbon particles. The effect of concentration over the short range investigated is small, as the data of table 4 show. Previously published data for salts

(1) show that the relationship between the potential of the suspended particle and the concentration of the dissolved salt is complex. In the range of concentration studied in this investigation, concentration is not an important factor in the value of the zeta potential, and as the data of table 4 show, no significant differences were observed. The concentrations investigated center about those used in laundry practice.

The data listed in both tables 3 and 4 are in agreement with a hypothesis that the negative ions or negatively charged ionic micelles of soaps are adsorbed by an inert surface. This, in itself, is not unexpected, for the adsorption of ions of salts by inert surfaces is a general phenomenon. However, in order for this adsorption to result in a stable suspension of the

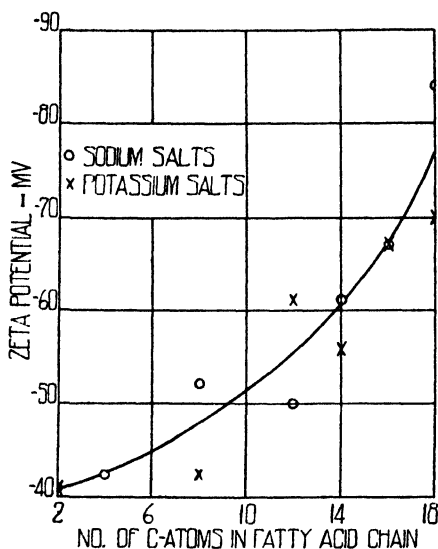


FIG. 1. Effect of increasing length of the fatty-acid chain on the zeta potential.

particles, the electric charge developed on the particles must be fairly high. Therefore, the magnitude of the effect of soaps on the zeta potential was compared with that of other salts.

In table 5 is shown the effect of salts containing negative ions of different valences on the zeta potential of the carbon particles suspended in their solutions. It is evident that the increase in potential produced by sodium oleate was appreciably greater than that produced by the other salts.

In table 6 are shown the values of the zeta potential obtained when the carbon was suspended in solutions of the sodium and potassium salts of some of the saturated fatty acids. These data are plotted in figure 1, showing that the effect on the zeta potential is greater with the salts of the higher homologs (the soaps) than with the lower members of the

series, and that the effect increases in a fairly regular order as the length of the carbon chain of the fatty acid increases.

Reference to table 7 shows that the alkalinity of the solutions of the sodium salts of the saturated fatty acid series increases with the length of the carbon chain of the fatty acid. It was necessary to determine whether the potentials observed for the soap solutions could be ascribed to this

TABLE 6

Zeta potentials obtained with sodium and potassium salts of certain fatty acids

COMPOUND, 0.0036 M	VELOCITY AT 75°C	ZETA POTENTIAL
	$\mu/\text{sec.}/\text{volt}/\text{cm.}$	millivolts
Sodium acetate.....	7 4	-41
Sodium butyrate.....	7 6	-42
Sodium caprylate.....	9 5	-52
Sodium laurate.....	9 1	-50
Sodium myristate.....	11 2	-61
Sodium palmitate.....	12 3	-67
Sodium stearate.....	15 4	-84
Potassium acetate.....	7 4	-41
Potassium caprylate.....	7 6	-42
Potassium laurate.....	11 2	-61
Potassium myristate.....	10 3	-56
Potassium palmitate.....	12 3	-67
Potassium stearate.....	12 7	-70

TABLE 7

pH of sodium salts of some of the fatty acids

COMPOUND, 0.0036 M	pH
Sodium acetate.....	7.8
Sodium butyrate.....	7.4
Sodium caprylate.....	7.6
Sodium laurate.....	8.3
Sodium myristate.....	10 0
Sodium palmitate.....	10.8
Sodium stearate.....	10.7

alkalinity. To do this, the effects of the addition of hydrochloric acid and of sodium hydroxide to solutions of sodium acetate and of sodium palmitate were determined. The data are listed in table 8.

The alkalinity of the soap solutions is not sufficient to account for their large effect on the zeta potential of the carbon particles suspended in them. The sodium acetate solutions did not have as great an effect as did similar solutions of sodium palmitate with the same concentration of hydroxyl

ions. One should note, however, that in order to obtain the high potential with sodium palmitate, it is necessary for the solution to be alkaline.

The effect of mixtures of fatty acids comprising the soap is shown in table 9. In this table are presented data obtained for soaps made from mixtures of oleic and stearic acids. It is apparent that there is no essential

TABLE 8

Effect of varying the pH of solutions of sodium acetate and of sodium palmitate on the zeta potential

(a) Sodium acetate, 0.0036 M				(b) Sodium palmitate, 0.0036 M			
pH	REAGENT ADDED	VELOCITY AT 60°C.	ZETA POTENTIAL	pH	REAGENT ADDED	VELOCITY AT 60°C	ZETA POTENTIAL
		$\mu/\text{sec.}/\text{volt}/\text{cm.}$	millivolts			$\mu/\text{sec.}/\text{volt}/\text{cm}$	millivolts
4 1	HCl	4 5	-30	2 8	HCl	3 9	-26
5 4	HCl	5 6	-38	3 8	HCl	7 0	-47
8 0		7 2	-49	4 7	HCl	7 4	-50
9 1	NaOH	7 5	-51	7 6	HCl	11 8	-80
10 0	NaOH	8 1	-55	8 5	HCl	10 1	-68
10 2	NaOH	7 5	-51	9 3	HCl	11 3	-72
11 4	NaOH	7.8	-53	10 1	HCl	11.3	-72
				10 8		10 3	-70

TABLE 9

Effect of soaps made from mixtures of oleic and stearic acids on zeta potential

STEARIC ACID IN FATTY ACID MIXTURE MAKING UP SOAP	VELOCITY AT 75°C.	POTENTIAL
per cent	$\mu/\text{sec.}/\text{volt}/\text{cm.}$	millivolts
0	13 2	-72
10	13 4	-73
20	14 9	-82
30	13 6	-75
40	14 4	-79
50	13 4	-73
60	14 2	-78
70	12 6	-69
80	13 2	-72
90	14 0	-77
100	15 4	-84

difference in the effects observed for the various mixtures. The potentials are of the same order of magnitude as those observed for pure sodium palmitate or stearate.

By the method described above (experimental procedure), a rough correlation was obtained between the stability of the suspension of the carbon

particles in various soap and salt solutions and the zeta potential. In figure 2 is shown a comparison between the potentials observed with the sodium salts of the fatty acid series (table 6) and the relative stability of the suspension of the carbon in solutions of the sodium salts of this series. Although the method of determining the stability was very rough, the relative order of the stabilities of the suspensions formed could be ascertained easily.

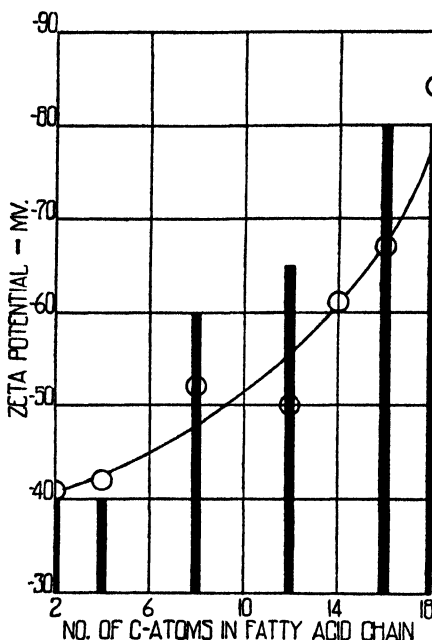


FIG. 2. A comparison of the values of the zeta potential with the stability of the suspension formed. The curve represents the values of the zeta potential for carbon particles immersed in the indicated solution. The heights of the heavy bars represent the stability of the suspension formed. The relative order of stability only is indicated.

Compared with the soaps, the inorganic salts listed in table 5 were not good suspending agents. This is in agreement with the relatively low zeta potentials observed.

DISCUSSION OF RESULTS

Emulsification of oily material and deflocculation of inert material constitute two of the primary functions of a detergent after the dirt has been removed from the surface to which it was attached. The data presented above indicate that soap solutions perform both of these important functions by essentially the same mechanism. The results indicate that

both the globules of an oil-in-water emulsion and the particles of a suspension of an inert material show an increase in the values of the zeta potential when a soap is present in the aqueous phase. This increase in potential is definitely larger than that observed with other salts. While the numerical value of the zeta potential is not always very much greater in the presence of a soap, nevertheless it is possible that only a certain critical potential must be reached to form a relatively stable suspension. Powis (12) has shown this to be true of emulsions. It also appears to be true for the carbon black investigated here. The value of this critical potential probably varies with the kind of material and size of the particles, according to Stokes' law.

This increase in the zeta potential must be due to the acquisition of the negatively charged constituents of the soap, either the single ions or, more likely, the ionic micelles postulated by McBain (7). The actual mechanism of the acquisition of these negative constituents may be different in the two cases. In the case of the emulsion of an oil, mutual solubility of the hydrocarbon tail of the fatty-acid ion of the soaps and of the oil may be the means of the acquisition. When inert materials are involved, an adsorption at the surface may take place, or a process involving the capillary action of the soap solution may occur. In either case, the result is apparently the same. The high charge resulting from the acquisition of the negative constituent of the soap stabilizes the emulsion or suspension, and in this way the dirt can be removed from the vicinity of the surface to which it was attached.

The deflocculating action of soap solutions has been suggested by McBain (8) and others as a means of evaluating the detergent powers of soaps. The methods proposed consist in the determination of the actual amount of a given material that can be held in suspension by a soap solution under certain standard conditions. If, as is here suggested, the ability of the soap solution to hold the material in suspension depends upon the magnitude of the effect on the zeta potential of the particles of the suspension, then measurement of the zeta potential affords a rapid method of evaluating a detergent. The ability to emulsify can also be determined in this way. However, the method will require considerable refinement to be of practical value.

SUMMARY

The effect of soaps on the zeta potential of the oil droplets of typical oil-in-water emulsions and on the zeta potential of certain "inert" materials has been investigated. In both cases the presence of soap increased the value of the (negative) zeta potential. Very high values of the zeta potential were obtained for oil globules of emulsions, and these are considered sufficiently high to account for the stability of the emulsions. The

zeta potentials of the particles of an inert material suspended in soap solutions were appreciably higher than those obtained in solutions of other salts. In the case of the salts of the fatty-acid series, over the range investigated, the potential increases with the length of the carbon chain of the fatty acid present in the salt. It has been shown that the free alkali present in soaps is not sufficient to account for the large effect of soaps on the zeta potential. At 75°C., soaps prepared from mixtures of oleic and stearic acids have the same effect as soaps prepared from the individual fatty acids.

It has been shown that soaps producing a high negative potential on certain carbon particles also form a stable suspension of the carbon. Conversely, salts which do not alter the potential of the carbon particles to any great extent do not form stable suspensions.

This effect of increasing the zeta potential of the oil droplets of an emulsion and of the particles of a suspension is suggested as the mechanism whereby soaps act as emulsifying and deflocculating agents.

Measurement of the effect of a solution of a soap on the zeta potential of the oil droplets of an emulsion or of the particles of a suspension is suggested as a means of evaluating the detergent powers of a soap.

Our thanks are due to Professor T. F. Young of the University of Chicago for his kind interest and advice in the preparation of this material for publication.

REFERENCES

- (1) ABRAMSON, H. A.: Colloid Symposium Monograph **1934**, p. 277. The Williams & Wilkins Co., Baltimore (1934).
- (2) BURTON, E. F.: Phil. Mag. **67**, 587 (1909).
- (3) ELLIS, R.: Z. physik. Chem. **78**, 321 (1912); **80**, 597 (1912); **89**, 145 (1914-15).
- (4) FERGUSON, R. H., AND RICHARDSON, A. S.: Ind. Eng. Chem. **24**, 1329 (1932).
- (5) GIBBARD, J.: Science **72**, 398 (1930).
- (6) GILFORD, C. L. S.: Phil. Mag. **19**, 853 (1935).
- (7) MCBAIN, J. W., AND SALMON, C. S.: J. Am. Chem. Soc. **42**, 426 (1920).
- (8) MCBAIN, J. W., HARBORNE, R. S., AND KING, A. M.: J. Soc. Chem. Ind. **42**, 373T (1923).
- (9) NORTHROP, J. H., AND KUNITZ, M. J.: J. Gen. Physiol. **7**, 729 (1924-25).
- (10) OLIN, H. L., LYKINS, J. D., AND MUNRO, W. P.: Ind. Eng. Chem. **27**, 690 (1935).
- (11) PICKERING, S. U.: J. Chem. Soc. **111**, 86 (1917).
- (12) POWIS, F.: Z. physik. Chem. **89**, 91, 179, 186 (1914-15).
- (13) SMITH, E. L.: J. Phys. Chem. **36**, 1401 (1932).
- (14) WYMAN, J., JR.: Phys. Rev. **35**, 623 (1930).

OPTICAL DIFFICULTIES WITH THE CYLINDRICAL CATAPHORESIS CELL

A. M. BUSWELL AND T. E. LARSON

Department of Chemistry, University of Illinois, Urbana, Illinois

Received May 29, 1936

In the cylindrical cataphoresis cell described by Mattson (1, 2) it should be of interest to know what optical precautions must be taken to obtain

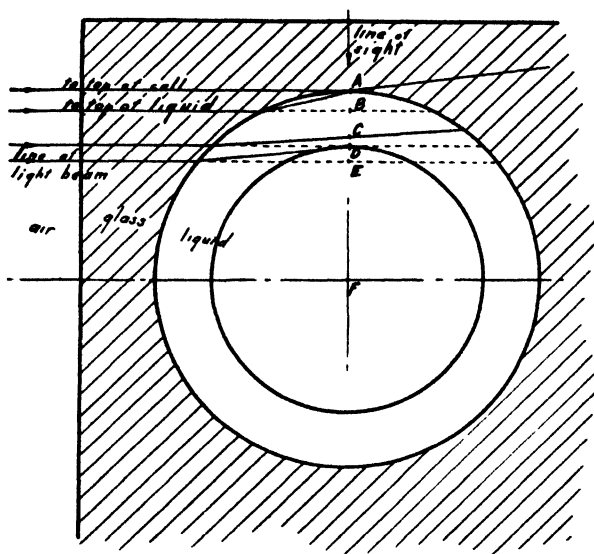


FIG. 1. Cylindrical cataphoresis cell. All depths are measured down from the top, A. D is the point or zone desired. AF is the radius of the cell. AD is $(R - R/\sqrt{2})$ or $0.293R$. AC is the depth observed when light enters the cell at the depth AD ($0.293R$). AD is the depth observed when light enters at the depth AE ($0.377R$). AB is the "blind spot," or the depths that cannot be seen until light enters at a depth greater than AB.

observations at the correct depth in the cell. This depth is that at which the velocity of the liquid due to endosmosis is zero and is calculated (2) to be $(R \text{ (radius)} - R/\sqrt{2})$, or $0.293R$ measured vertically down from the top of the solution in the cell.

If the light beam enters the front of the cell at this depth and the microscope is focused on the beam in the cell, the observations made on the

cataphoretic velocities of the particles do not represent the true velocities unaffected by the velocity of the liquid. The light beam does not pass from the glass to the liquid normal to the interface, and the refractive index of the glass is appreciably different from that of the water which is usually the continuous phase of the sol. Thus, the light beam is bent upward (figure 1) to a depth of $0.195R$ from the top, midway between the front and back of the cell. To obtain illumination at the correct depth, the light beam should enter the liquid at a depth of $0.377R$.

The index of refraction of water and glass have been taken as 1.342 and 1.515, respectively, for the above calculations. If n_p for water were 1.35, owing to the salt content, the resulting discrepancy is but slightly different from that calculated. It is interesting to note that in the zone (0 to 0.114) R , there is a "blind spot" where the particles should not be observed, since the light beam is reflected outside the glass-water interface. It should also be noted that the front air-glass interface should be perpendicular to the light beam, or the possibility of error in the position of the light beam in the cell will be increased.

REFERENCES

- (1) MATTSON, S.: J. Phys. Chem. **32**, 1532 (1928).
- (2) MATTSON, S.: J. Phys. Chem. **37**, 223 (1933).

SURFACE SPREADING AND SURFACE SOLUTION OF POSITIVELY ADSORBED SUBSTANCES

T. F. FORD

Department of Chemistry, Stanford University, California

Received May 29, 1936

It was observed by Miss Pockels (1) that various substances when touched to clean talc-dusted water surfaces cause streaming motions outward from the point of contamination. Although she did not then distinguish explicitly between the behavior of soluble and insoluble substances, in a later paper (2) it is clear that she considered the process of surface spreading essential to the phenomena of positive adsorption. In continuing and extending Miss Pockels' experiments, using soluble substances, we have found that all of those that lower the surface tension of water spread in the surface to form films, this surface spreading being an intermediate step in the process of solution. Thus, a fragment of hydrocinamic acid, or a droplet of phenol, or of caprylic acid touched to a talc-dusted water surface immediately produces a circular patch cleared of talc, exactly as if an insoluble spreading oil had been applied, and on removal of the source this patch quickly contracts and disappears. A surface may be completely contaminated in this way many times and no permanent film result, showing that the momentary contamination was due to the soluble material alone. The same phenomenon occurs with camphor on water, and, as further examples, with the following substances: acetic acid, gelatin, aniline, hydrogen chloride, ethyl alcohol, abietic acid, benzamide, ammonia, ethyl acetate, potassium laurate, benzoic acid, sodium silicate, acetone, triethanolamine, hydroquinone, carbon dioxide.

This process of surface solution is extremely rapid, undoubtedly because the substances spread out into films against limitless boundaries, there rapidly achieving maximum extenuation and contact with water short of actual solution. In these films the area available for escape of individual molecules has been enormously increased. Whether solution actually occurs at a greater rate per unit area of monomolecular film than of submerged surface is not known. As expected, however, completely submerged droplets, or fragments, which have no surfaces available into which their oriented surface layers can spread, dissolve very slowly. The great difference in the rate of solution of certain partially immersed solid substances at the water surface and beneath it has been observed by Pockels

(2) and by Volmer and Mahnert (4) and by others. We have found a striking demonstration of this fact by use of a droplet of phenol, which if submerged in water will remain apparently unchanged for several hours, but if brought into the surface will spread and completely dissolve in a fraction of a second; or by observing the surface of a fine aqueous suspension of hydrocinnamic acid, in which random, spontaneous areas of spreading—"Pockels" (5)—appear, evidently caused by arrival in the surface of wandering particles previously submerged and undissolving.

Surface solution is a factor even in the dissolving of submerged fragments, because particles break off from the crystal mass as observed by Traube (3) and wander away, owing to Brownian motion and convection currents and perhaps owing to reaction of their escaping surface molecules against both particle and solution, and eventually enter the surface where they disperse by spreading. In confirmation of this, observations of clean water surfaces beneath which crystals of hydrocinnamic acid were submerged disclosed "Pockels" exactly similar to those obtained with the hydrocinnamic acid suspension previously referred to.

Many substances are dissolved in the industries by putting them on trays near the surface of water, thus utilizing the stirring action resulting from changes in density to accelerate the process of solution. In the case of materials like phenol, surface spreading is perhaps often another important, and unrecognized, factor in hastening the rate of solution. Obviously, such materials should be partly exposed above the surface.

In considering the relation between adsorption and surface tension, the mechanism of surface solution assumes theoretical importance in view of Miss Pockels' belief that solutions of all capillary-active substances are colloidal or subcolloidal in nature (2), and of Traube's ultramicroscopic evidence (3) that subcolloidal particles, or "microns", represent an intermediate stage both in the dissolving of crystals and in the growth of crystals from solution, and that they may even enjoy a stable existence in solutions of many substances.

REFERENCES

- (1) POCKELS, A.: *Nature* **43**, 437 (1891).
- (2) POCKELS, A.: *Naturwissenschaften* **9**, 137 (1917); **10**, 149 (1917).
- (3) TRAUBE, J., AND BEHREN, W.: *Z. physik. Chem.* **138A**, 85-101 (1928).
- (4) VOLMER, M., AND MAHNERT, P.: *Z. physik. Chem.* **115**, 239-52 (1925).
- (5) WILSON, D. A., AND FORD, T. F.: *Nature* **137**, 235 (1936).

A COMPARISON OF THE GLASS AND QUINHYDRONE ELECTRODES FOR THE MEASUREMENT OF THE ACTIVITY OF THE HYDROGEN ION IN SUCROSE SOLUTIONS

H. P. CADY AND J. D. INGLE

Department of Chemistry, University of Kansas, Lawrence, Kansas

Received February 21, 1936

INTRODUCTION

In the determination of the activity of the hydrogen ion in acidified sucrose solutions by electromotive force methods, the hydrogen electrode has been used by a number of investigators, including W. C. M. Lewis and his associates (1, 3, 6), Taylor and Bomford (9), who found that the hydrogen-ion activity increases during the inversion of sucrose by acid, and by Seatchard (8), who found that the hydrogen electrode does not give reliable values of the hydrogen-ion activity in sucrose solutions.

We thought that the glass electrode (2, 5) might be used to measure accurately the activity of the hydrogen ion in sucrose solutions. We used the quinhydrone electrode for comparison.

EXPERIMENTAL PROCEDURE

Silver-silver chloride electrodes were used as standard reference electrodes. They were prepared as suggested by MacInnes and Beattie (4).

The glass electrodes were prepared as recommended by MacInnes and Belcher (5). The quinhydrone electrodes used were flat pieces of platinum, 2 x 1 cm. All of the solutions used in the measurements were 0.1 molal with respect to hydrochloric acid and 0.1 molal with respect to the other constituent, either sucrose, dextrose, or levulose. All of the measurements were carried out at 30°C.

APPARATUS

The electrical measurements made using the quinhydrone electrode were made with a Leeds and Northrup Type K potentiometer and a Leeds and Northrup high sensitivity Type R galvanometer.

The electrical measurements using the glass electrode were made with a circuit including a space charged grid tube, the G.E.F.P. 54 Plotron. A diagram of this circuit is shown in figure 1.

The glass cell used in making measurements of E.M.F. between the silver-

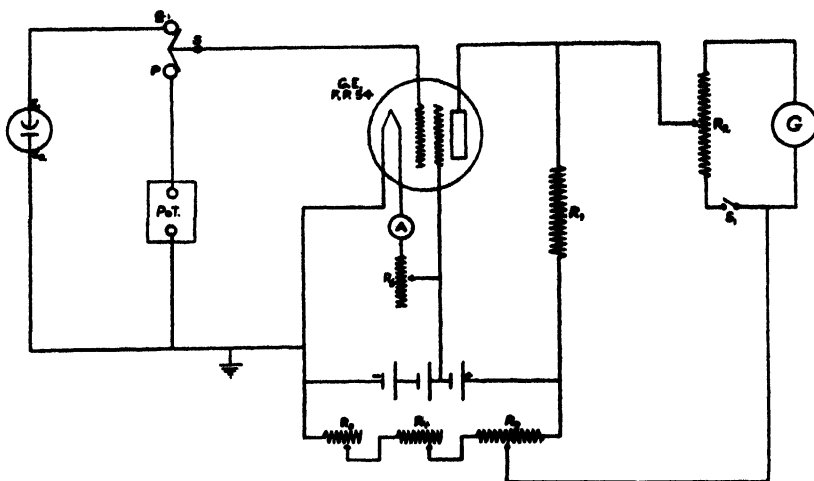


Fig. 1. Diagram of the circuit

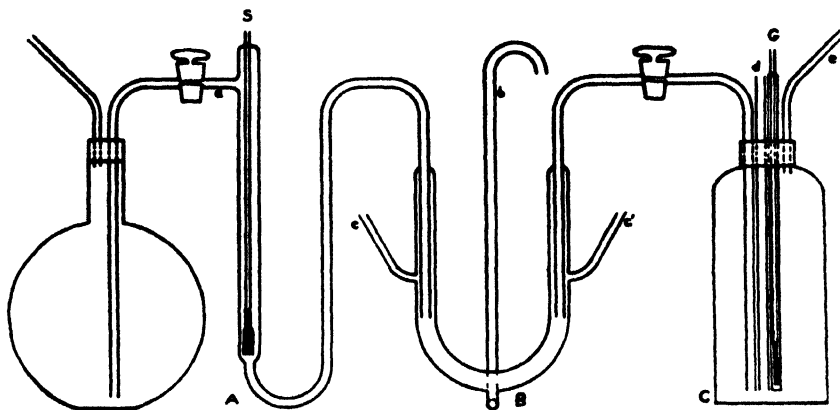


Fig. 2. Glass cell used in making measurements of E. M. F. between the silver-silver chloride half-cell and the glass electrode

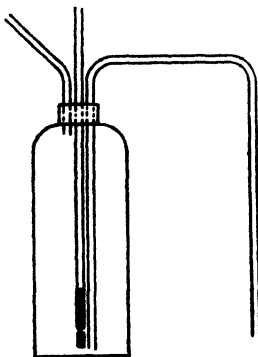


FIG. 3. The half-cell used in the experiments involving a number of electrodes

silver chloride half-cell and the glass electrode is shown in figure 2. The first series of measurements with the quinhydrone electrode was made in this cell.

The half-cell used in the experiments involving a number of electrodes is shown in figure 3.

TABLE 1

E. M. F. measurements with the cell

Pt	0.1 <i>M</i> Sucrose 0.1 <i>M</i> HCl Quinhydrone	0.1 <i>M</i> HCl	0.1 <i>M</i> HCl	Ag-AgCl	
TIME		EMF	TIME		EMF.
<i>hrs</i>	<i>mins</i>	<i>volts</i>	<i>hrs.</i>	<i>mins</i>	<i>volts</i>
	10	0 3456	27	30	0 3446
	30	0 3455	33	30	0 3443
1	30	0 3454	43	30	0 3436
3	30	0 3454	47	30	0 3434
6	30	0 3454	53	30	0 3432
18	30	0 3448	66	30	0 3423
24	30	0 3446	72		0 3419

TABLE 2

Measurements made between pairs of platinum electrodes immersed in 0.1 molal hydrochloric acid containing quinhydrone

TIME		E M F. IN MILLIVOLTS																			
		I		II		III		IV		V		VI		VII		VIII		IX		X	
		A	F.	A.	L	A	D	A	Ivd S	Ivd S.	F	Ivd S	D	Ivd S.	L	D	L	D	F.	L.	F.
hrs	mins																				
	30			0 487		0 287		0 248				0 039		0 239		0 200					
1	5			0 177		0 175		0 321				-0 146		-0 144		0 002					
1	30	-0 035		0.180		0 144		0 303		-0.512		-0 159		-0 123		0 036		-0 179		-0 215	
2	10	0.062		0.209		0.130		0 303		-0.364		-0 172		-0.094		0 079		-0 068		-0 147	
2	30	-0 094																			
3	45	0 065		0 211		0 164		0 303		-0 277		-0 149		-0 092		0.057		-0 089		-0 146	
4	25	0 029																			
6	45	0.380		0.224		0 213		0.304		-0 038		-0 091		-0 080		0 011		0 167		0 156	
16	45	0.246																			
23	45	1 465		0 173		0 115		0 164		1 166		-0 049		0.009		0 058		1 350		1 292	
30	25	1.393																			
42	45	2.962		0.206		0.126		-0 070		2.820		0.196		0 276		0 080		2.836		2.756	

DATA

The data in table 2 represent measurements made between pairs of platinum electrodes immersed in 0.1 molal hydrochloric acid containing

TABLE 3
Measurements of *E. M. F.*

TIME		E. M. F. IN VOLTS									
		I		II		III		IV		V	
		F.	Ag	F.	A.	Ivd. S.	Ag	Ig. S.	Ag	A.	Ag
hrs.	mins.										
	20	0.34377		-0.00100		0.34521		0.34304		0.34476	
	50	0.34409		-0.00058		0.34507		0.34491		0.34467	
1	50	0.34431		-0.00033		0.34496		0.34480		0.34456	
3	20	0.34429		-0.00023		0.34488		0.34473		0.34449	
7	35	0.34450		0.00021		0.34469		0.34459		0.34425	
21	35	0.34463		0.00120		0.34395		0.34387		0.34338	
31	35	0.34494		0.00225		0.34338		0.34323		0.34260	
55	35	0.34495		0.00491		0.34116		0.34104		0.33996	
72		0.34516		0.00719		0.33973		0.33948		0.33790	
		VI		VII		VIII		IX		X	
		A.	Ivd. S.	A.	Ig. S.	Ig. S.	Ivd. S.	Ig. S.	F.	Ivd. S.	F.
	20	0.00045		0.00028		0.00017		-0.00127		-0.00144	
	50	0.00040		0.00024		0.00016		-0.00082		-0.00098	
1	50	0.00040		0.00024		0.00016		-0.00049		-0.00065	
3	20	0.00039		0.00024		0.00015		-0.00044		-0.00059	
7	35	0.00044		0.00029		0.00010		-0.00009		-0.00019	
21	35	0.00057		0.00049		0.00008		0.00076		0.00068	
31	35	0.00078		0.00063		0.00015		0.00171		0.00156	
55	35	0.00120		0.00108		0.00012		0.00391		0.00379	
72		0.00183		0.00158		0.00025		0.00568		0.00543	

TABLE 4
E. M. F. measurements using a glass electrode

Ag, AgCl	0.1 M HCl	0.1 M HCl	0.1 M HCl Glass 0.1 M inverting Sucrose	Ag, AgCl 0.1 M HCl
TIME IN HOURS		E. M. F. IN MILLIVOLTS		
		Trial I		Trial III
	0.5	0.44		0.45
	1.5	0.45		0.41
	3.5	0.42		0.40
	7.5	0.42		0.42
	21.5	0.43		0.48
	31.5	0.36		0.43
	43.5	0.42		0.40
	51.5	0.44		0.46
	72.0	0.40		0.43

quinhydrone. All pairs of electrodes were connected by liquid bridges of 0.1 molal hydrochloric acid. Substances added to the cells are indicated at the top of each column. F stands for "freshly prepared electrode", D for "dextrose", L for "levulose", Ivd. S. for "inverted sucrose", and A indicates "the original acid and quinhydrone with nothing added". All substances added had concentrations of 0.1 molal.

The symbols used in table 3 are the same as those in table 2. The additional symbol Ig.S., meaning "inverting sucrose", is also used. Ag is used to indicate a Ag-AgCl electrode in 0.1 molal hydrochloric acid, in place of a quinhydrone electrode.

DISCUSSION

The data in table 1 indicate a large apparent decrease in the hydrogen-ion activity during the acid inversion of sucrose. Such a large decrease in the activity, however, appears improbable.

The data in tables 2 and 3 show that the potential of a quinhydrone electrode in old hydrochloric acid solution changes with the passage of time.

The data in tables 2 and 3 also show that the inverting sucrose, the inverted sucrose, the dextrose, and the levulose all have about the same effect upon the potential of a quinhydrone electrode. In fact they seem to affect the potential of the electrode very little.

The data in columns III, IV, and V of table 3 indicate that the potential of the quinhydrone electrodes in the old hydrochloric acid solution, the inverting sucrose, and the inverted sucrose solutions, all become less positive with respect to the silver-silver chloride half-cell as time passes. Now since the potential of the quinhydrone electrode depends solely upon the activity of the hydrogen ion and the ratio of the activity of the quinone to the activity of the hydroquinone, and since it is not probable that the activity of the hydrogen ion has changed in this closed system, it is evident that the drop in potential must be due to a decrease in the above-mentioned ratio to some value less than unity. Thus either the activity of the quinone must have decreased or the activity of the hydroquinone must have increased. Now the quinone is known to be a fairly strong oxidizing agent; it can add hydrochloric acid in a concentrated solution of hydrochloric acid. Biilmann has shown that the change in potential of the quinhydrone electrode in dilute hydrochloric acid solutions is due to some action of the hydrochloric acid on quinone. This being the case, the activity of the quinone would be reduced and the voltage of the electrode would be reduced. Since the decrease in potential for the electrodes in the inverting and inverted sucrose solutions is so very nearly the same, we can conclude that the formation of the inversion products of sucrose has little or no effect on the potential of the quinhydrone electrode. This also indicates

that it makes no difference whether the inversion products are all present at once or whether they are formed in the acid solution as time goes by. Since the only other substance present is the hydrochloric acid, we must assume that it is the hydrochloric acid that is causing the change in potential of the electrode. This is also borne out by the fact that the old hydrochloric acid solution which was in contact with the quinhydrone for three days showed an even more pronounced effect upon the potential of the electrode than did the solutions which contained the inversion products of sucrose. The fact that the electrode in the inverting and inverted sucrose solutions gave a constant difference of potential during the whole seventy-two hours, would indicate that the rate of change of potential of both electrodes is the same. The data in column VIII of table 3 show the truth of the above statement.

Columns VI and VII of table 3 indicate that the potential of the electrode in the old hydrochloric acid solutions becomes less positive more rapidly than does the potential of either the electrode in the inverting or that in the inverted sucrose solutions.

The data in column VIII of table 2 indicate that the rate of change of potential of the quinhydrone electrode in a solution containing levulose is the same as that for an electrode in a solution containing dextrose. Thus the data of tables 2 and 3 indicate that the products of inversion of sucrose have little or no effect, either separately or collectively, upon the potential of the electrode.

The data in column I of table 3 confirms the conclusions of Morgen, Lamert, and Campbell (7), i.e., the potential of the quinhydrone electrode can be accurately reproduced only when care is taken to clean and dry the electrode before use. In our experiments the electrode after use in the acidified quinhydrone solution was left in the solution until time for the next measurement on a fresh solution, at which time it was washed with distilled water and transferred to the freshly prepared quinhydrone solution. It may be seen that the potential of the electrode, used in the above manner, showed an increase. This would indicate that the amount of oxidation, i.e., the oxidizing agent, in the cell had increased. Now each time the electrode was placed in a fresh solution, the electrode came in contact with the air; also the solution was thoroughly shaken to dissolve the quinhydrone quickly. If oxygen from the air were absorbed on the platinum surface there is a possibility that some hydroquinone was oxidized to quinone and thus the potential of the electrode was slightly raised.

The data in table 4 show that the E.M.F. of the glass electrode with respect to the silver-silver chloride half-cell remains constant throughout the acid inversion of sucrose. Since the E.M.F. remained constant throughout the inversion, it follows that the activity of the hydrogen ion remained constant also. Thus it is seen that the hydrogen ion is a true catalyst in

this reaction. The work of Taylor and Bomford (9) showed an increase in the activity of the hydrogen ion during the inversion process, but this is undoubtedly due to the hydrogenation of the sucrose, as suggested by Scatchard (8).

SUMMARY

1. The quinhydrone electrode has been used to measure the activity of the hydrogen ion in inverting sucrose solutions and has been found to give a changing potential when the electrode is left in contact with the acidified quinhydrone solution for long periods of time.

2. The glass electrode has been used to measure the activity of the hydrogen ion in inverting sucrose solutions and has been shown to give reproducible results.

3. By the use of the glass electrode it has been shown that the activity of the hydrogen ion remains constant throughout the inversion of sucrose by hydrochloric acid.

REFERENCES

- (1) CORRAN AND LEWIS: J. Am. Chem. Soc. **44**, 1673 (1922).
- (2) DOLE: J. Am. Chem. Soc. **54**, 3095 (1932).
- (3) JONES AND LEWIS: J. Chem. Soc. **117**, 1120 (1920).
- (4) MACINNES AND BEATTIE: J. Am. Chem. Soc. **42**, 1117, 1455 (1920).
- (5) MACINNES AND BELCHER: J. Am. Chem. Soc. **53**, 3315 (1931).
- (6) MORAN AND LEWIS: J. Chem. Soc. **121**, 1613 (1922).
- (7) MORGEN, LAMMERT, AND CAMPBELL: J. Am. Chem. Soc. **53**, 454 (1931).
- (8) SCATCHARD: J. Am. Chem. Soc. **48**, 2026 (1926).
- (9) TAYLOR AND BOMFORD: J. Chem. Soc. **125**, 2016 (1924).

THE ACTIVITY COEFFICIENTS OF LITHIUM CHLORIDE AND POTASSIUM IODIDE IN ETHYL ALCOHOL BY THE BOILING-POINT METHOD

J. N. PEARCE AND M. L. McDOWELL

The Physical Chemistry Laboratory of the State University of Iowa, Iowa City, Iowa

Received April 24, 1936

This paper presents the results obtained in an attempt to determine the activity coefficients of strong electrolytes in non-aqueous solvents by the boiling-point method. The apparatus and the technique employed are practically the same as that described in our previous paper (8).

Although the major features of the familiar Cottrell-Washburn apparatus (2, 11) have been retained, two important changes have been made. We have substituted for the troublesome gas flame a more uniform and constant source of electrical heating. Sealed into the bottom of each boiling flask is a coil of No. 30 platinum wire; these coils are of exactly the same length and resistance, thus insuring the introduction of equal amounts of heat into each flask when these are joined in series with the lighting circuit. The fine wire spiral furnishes an ideal surface for easy and rapid bubble formation which, together with the rapid flow of the liquid over the spiral, makes superheating practically impossible. The funnels, provided with slits at the bottom and several lateral openings, are placed concentric with the spirals. Under steady boiling the bubbles rising through the tube and those passing laterally through the funnel not only insure constant thermal equilibrium, but also keep the solution homogeneous by rapid agitation. Two boiling vessels are used. Instead of thermometer bulbs, the liquid from the pump flows over a test tube containing mercury in which is placed one arm of a 50-junction thermoelement. One flask containing the pure boiling solvent serves as the "cold" junction.

Bancroft and Davis (1) contend that superheating in the Cottrell apparatus is largely due to the hydrostatic pressure under which the bubbles are formed. They state that, if this superheating is removed in part by the passage of the bubbles through a mass of the solution before entering the pump, it should be further diminished in its subsequent passage through the pump. In their modification of the original Cottrell apparatus, the funnel, instead of resting upon the bottom of the flask, rests upon a constriction in the wall of the boiling flask at several inches above the bottom. In spite of the fact that they still use the gas flame for heating, they claim

that the superheating of the solution and the effect due to hydrostatic pressure are completely eliminated in their apparatus. More recently, in a study of the activity coefficients of aqueous solutions of potassium chloride, Saxton and Smith (10) have devised two new forms of the Cottrell apparatus,—one for gas and one for electrical heating. Their claims for the removal of superheating are equally good.

APPARATUS AND MATERIALS

The complete apparatus, including the "K 2" potentiometer and galvanometer, were carefully shielded. A current of 6.2 amps. was maintained through the heating coils during operation.

Three thermoelements were prepared according to the specifications of White (12), one with fifty junctions and two with ten junctions each. These were standardized against a platinum resistance thermometer (Bureau of Standards, No. 292) in conjunction with a Mueller bridge and high sensitivity galvanometer. The fixed points were those of liquid oxygen, liquid ammonia, ice, the transition point of sodium sulfate decahydrate, and the boiling point of water.

Since the 50-junction element was to be used for the determination of small temperature increments near the boiling point of alcohol, it was first necessary to calibrate it for that range also. This necessitated the employment of a triangular arrangement of the three thermoelements. The two boiling flasks were filled to the working volume with pure alcohol, connected by means of the 50-junction element, and the alcohol heated to boiling. Each flask was connected in turn with the Dewar ice calorimeter by a 10-junction element. The solvent was allowed to boil in each flask until the potential of the connecting thermoelement became constant. At this point the potentials of the 10-junction elements were read, and from these potentials the apparent difference in the boiling point of the solvent in the two flasks was calculated. This potential difference, due probably to inequalities in the arms of the element, was used in correcting all subsequent thermoelement potentials.

To obtain the temperature intervals for deducing an equation relating temperature and potential at the boiling point of the alcohol, both flasks were filled to the proper volume with pure benzene; to one of these was added later successive portions of pure naphthalene. In each case the boiling was continued until the potential of the 50-junction element became constant. The potentials of the two smaller elements were read immediately and the boiling temperatures were calculated. From the boiling-point elevation thus determined we derived a potential-temperature equation for the 50-junction element in the vicinity of the boiling point of ethyl alcohol. A table was constructed by solving the equation for potentials corresponding to 0.1°C. intervals, and from these the exact temperature for any measured potential was easily interpolated.

Thiophene-free benzene, b.p. 80.17°C., absolute ethyl alcohol, b.p. 78.82°C., and naphthalene, m.p. 80.08°C., were prepared according to accepted methods. The two salts were repeatedly crystallized from pure distilled water. The potassium iodide was heated to constant weight at 140°C. just before it was used. The lithium chloride crystals were first heated in a current of dry hydrogen chloride gas until all traces of water were removed. The heating was then continued in a current of dry hydrogen to remove all traces of acid. The salts were transferred to the alcohol in the flasks without contact with the atmosphere.

The dried salts were dissolved in alcohol in the apparatus to approximate saturation at the boiling point, and the resulting solutions were used for the first measurements. The constant potential indicating thermal equilibrium, corrected by the zero reading of the element, supplied the necessary data for calculating the boiling-point elevation. Under a pressure of dry air samples of the solution were withdrawn for analysis into tared glass-stoppered flasks and weighed immediately. After a sample was removed sufficient pure alcohol was added to maintain a constant solution volume, thus making a new concentration for the next measurement. The salt content of the solution was determined volumetrically by the Volhard method. The concentrations are expressed in moles per 1000 grams of solvent.

EXPERIMENTAL RESULTS

The experimental results are collected in table 1. Here m is the molality of the salt, θ is the elevation of the boiling point, and θ/m is the molal elevation of the boiling point of the solvent. The values of θ/m for lithium chloride pass through a distinct minimum value; except for the most dilute solutions, the molal elevation of the boiling point of alcohol by potassium iodide remains practically constant throughout the whole range of concentration.

According to Raoult's law, the boiling-point elevation of a solvent by an ideal non-electrolyte should be directly proportional to the mole fraction of the solute, or to $n_2/(n_1 + n_2)$. If we assume, however, complete dissociation for a binary salt and that the ions behave as perfect solutes, the boiling-point elevation should be proportional to $2n_2/(n_1 + 2n_2)$. That is,

$$\theta = \frac{RT_b^2}{\Delta H_v} \frac{2n_2}{n_1 + 2n_2}$$

The relation between the boiling-point elevation and the molality for the two salts is shown graphically in figure 1. The broken lines represent the theoretical curves for non-electrolyte and completely dissociated salt, both assumed to be perfect solutes. Although the salts are completely ionized in the crystalline state and in solution, the relations obtained for dilute

TABLE 1

Elevation of the boiling point of ethyl alcohol by electrolytes

m	θ°	θ/m	m	θ°	θ/m	m	θ°	θ/m
(a) Lithium chloride								
0.01266	0.01535	1.2124	0.18017	0.22149	1.2293	0.41117	0.55145	1.3412
0.02328	0.02823	1.2126	0.20126	0.24871	1.2358	0.44001	0.59663	1.3559
0.04051	0.04879	1.2044	0.24234	0.30508	1.2589	0.44958	0.61244	1.3622
0.07227	0.08589	1.1884	0.27085	0.34351	1.2653	0.49303	0.68027	1.3797
0.11023	0.13108	1.1891	0.28707	0.36613	1.2756	0.57580	0.81587	1.4169
0.13115	0.15596	1.1892	0.37098	0.48366	1.3037	0.66213	0.95370	1.4404
0.15874	0.19431	1.2241						
(b) Potassium iodide								
0.01016	0.01246	1.2364	0.07003	0.08507	1.2148	0.12420	0.14984	1.2054
0.01662	0.02033	1.2232	0.07806	0.09523	1.2200	0.13796	0.16695	1.2101
0.02454	0.02956	1.2326	0.08730	0.10589	1.2130	0.14939	0.18037	1.2074
0.03822	0.04713	1.2331	0.09378	0.11467	1.2228	0.15696	0.19054	1.2139
0.05173	0.06332	1.2241	0.10657	0.12814	1.2024			
0.06010	0.07390	1.2297	0.12238	0.14754	1.2056			

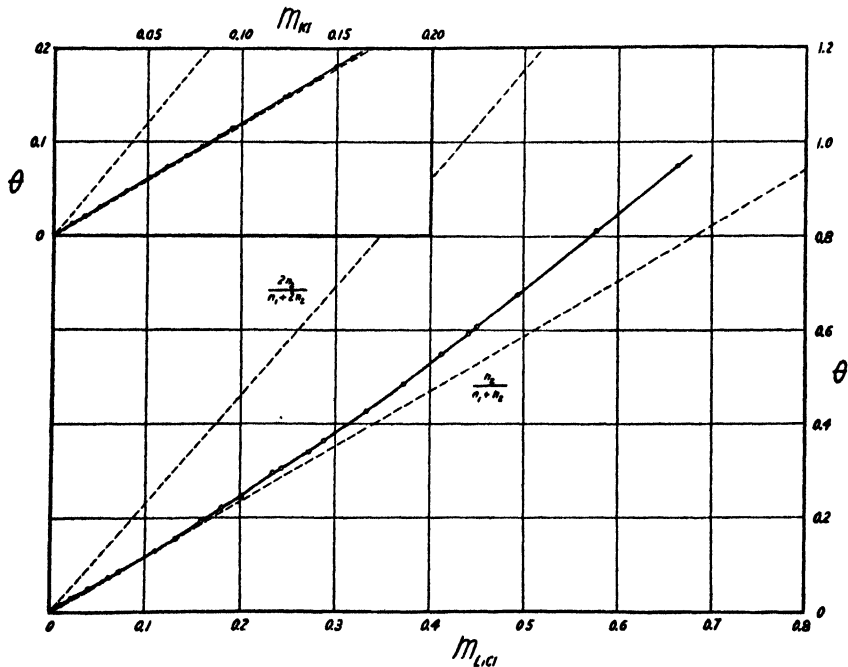


FIG. 1

solutions correspond closely with those which would be produced by undissociated solute molecules. The larger deviations from the normal boiling-point elevations in the more concentrated solutions indicate a rather decided increase in the number of free ions present. Since we have assumed that the salts are completely ionized at all concentrations, the approximation to the behavior of perfect normal undissociated solute molecules can be explained best by assuming the existence of simple or chain ions in equilibrium with paired ions or quadripoles. The formation of ion pairs and quadripoles is especially favored in solvents with low dielectric constants. The dielectric constant of ethyl alcohol (3) decreases from 28.9 at 20°C. to 20.2 at 60°C. Its unknown value at the boiling point must be still smaller.

Following the method of Lewis and Randall (5) for freezing-point work we may calculate the activity of the solvent from boiling-point elevation data. The influence of temperature on the activity of the solvent in the vicinity of the boiling point is given by the relation,

$$d \ln a_1 = - \frac{\Delta H}{RT^2} dT \quad (1)$$

If we designate by θ the elevation of the boiling point and by T_0 the boiling point of the pure solvent, the boiling point of the solution T is $T = T_0 + \theta$, and $dT = d\theta$. Expressing ΔH at the boiling point as a function of the temperature:

$$\Delta H = \Delta H_{T_0} + \Delta C_p \theta$$

and substituting in equation 1, we obtain

$$d \ln a_1 = - \frac{[\Delta H_{T_0} + \Delta C_p \theta]}{R(T_0 + \theta)^2} d\theta \quad (2)$$

By expanding the right-hand member, collecting terms, and neglecting terms of higher order, equation 2 becomes

$$d \ln a_1 = \frac{d\theta}{RT_0^2} \left[- \Delta H_{T_0} + \left(\frac{2\Delta H_{T_0}}{T_0} - \Delta C_p \right) \theta \dots \right] \quad (3)$$

Here, $T_0 = 351.4^\circ\text{K.}$, $\Delta H_{T_0} = 9414.2$ cals. (4), and $\Delta C_p = -17.320$ cals. The molal heat capacity of alcohol at its boiling point (35.173 cals.) was calculated by means of the relation (13): $C_p = 0.5068 + 0.00286t + 0.0000054t^2$; that of the vapor (17.853 cals.) by the equation (7): $C_p = 4.5 + 0.038T$. Introducing numerical values in equation 3, we obtain

$$d \ln a_1 = -0.03834 d\theta + 0.00028875 \theta d\theta \quad (4)$$

Upon integrating between the boiling point of the pure solvent, where $\theta = 0$, and the boiling point of the solution, and converting to common logarithms we obtain

$$\log a_1 = -0.016648 \theta + 0.000062688 \theta^2 \quad (5)$$

The activities of the alcohol, a_1 , in the various solutions are given in table 2.

The activity of the salt, a_2 , and that of the solvent, a_1 , are combined in the relation

$$d \ln a_2 = -\frac{N_1}{N_2} d \ln a_1 \quad (6)$$

where N_2 and N_1 are the respective mole fractions. Combining equations 4 and 6 and substituting molalities for mole fractions, we obtain

$$d \ln a_2 = \frac{21.717}{m} (0.03834 - 0.00028875\theta) d\theta \quad (7)$$

For the case where θ approaches zero the last term disappears. Since we are approaching infinite dilution we may write $a_2 = m$ and equation 7 reduces first to

$$d \ln m = \frac{dm}{m} = \frac{21.717}{m} 0.03834 d\theta \quad (8)$$

which by rearranging gives for the molal elevation of the boiling point of ethyl alcohol at infinite dilution,

$$\lambda = d\theta/dm = 1.2010^\circ \quad (8')$$

This value is slightly lower than the value, 1.240° , given by Rosanoff and Dunphy (9).

By inserting the value of λ in equation 7 we obtain an expression for calculating the activity of any non-dissociating solute, namely,

$$d \ln a_2 = \frac{d\theta}{\lambda m} - \frac{0.006271}{m} \theta d\theta \quad (9)$$

Since $a_2 = a_{\pm}^\nu$, it is evident that for any electrolyte giving ν ions per mole,

$$d \ln a_{\pm} = \frac{d\theta}{\nu \lambda m} - \frac{0.006271}{\nu m} \theta d\theta \quad (10)$$

To integrate this expression Lewis and Randall (6) have invented a j -function which rapidly approaches zero at infinite dilution, that is,

$$j = 1 - \theta/\nu \lambda m.$$

Following their procedure for the freezing-point method we obtain finally for the activity coefficients of the ions of binary electrolytes in ethyl alcohol the relation,

$$\log \gamma = -0.4343 \int \frac{j}{m} dm - 0.4343 j - 0.001362 \int \frac{\theta}{m} d\theta \quad (11)$$

To calculate the values of the activity coefficients, γ , it was first necessary to construct a large scale plot of θ against m . From this the values of θ/m , j , and j/m were calculated for round concentrations. Plots of j/m against m , and of θ/m against θ were drawn and the values of the two integrals in equation 11 were determined by means of a polar planimeter.

TABLE 2
Final data at round concentrations for ethyl alcohol solutions

m	θ°	a_1	γ	m	θ°	a_1	γ
(a) Lithium chloride							
0 01	0 01215	0 9989	0 1437	0 30	0.3860	0 9666	0.0276
0 02	0 0242	0 9978	0 1025	0 35	0.4586	0 9604	0 0258
0 05	0 0602	0 9947	0 0631	0 40	0 5345	0 9541	0 0245
0 10	0.1203	0 9894	0.0463	0 45	0 6121	0 9476	0 0235
0 15	0.1825	0 9843	0 0379	0 50	0 6909	0 9411	0.0225
0 20	0 2475	0 9784	0.0330	0 55	0 7724	0 9344	0 0218
0 25	0 3156	0 9726	0 0298	0 60	0 8541	0 9278	0 0212
				0 65	0 9376	0 9211	0 0207
(b) Potassium iodide							
0.01	0 0122	0 9989	0 1446	0 075	0 0907	0 9920	0 0539
0 02	0 0244	0 9978	0 1035	0 100	0 1207	0 9894	0 0469
0 05	0 0605	0 9947	0 0639	0 125	0 1511	0 9867	0 0420
				0 150	0 1815	0 9841	0.0382

The activity coefficients of the two salts in ethyl alcohol thus determined are collected in table 2.

In spite of the fact that we may assume that both salts are completely ionized at all concentrations, the activity coefficients of the ions of both salts are surprisingly low. While the activity of the alcohol is almost identically the same for equal concentrations of the two salts, the activity coefficients of the ions of potassium iodide are slightly higher than those of lithium chloride.

It would be interesting to calculate the activity coefficients of the ions on the basis of the Debye-Hückel theory. In the absence of knowledge of the ionic radii and of the dielectric constant of alcohol at the boiling point this is impossible.

REFERENCES

- (1) BANCROFT AND DAVIS: *J. Phys. Chem.* **33**, 591 (1929).
- (2) COTTRELL: *J. Am. Chem. Soc.* **41**, 721 (1919).
- (3) International Critical Tables, Vol. VI, p. 85. McGraw-Hill Book Co., Inc., New York (1929).
- (4) International Critical Tables, Vol. V, pp. 137-138. McGraw-Hill Book Co., Inc., New York (1929).
- (5) LEWIS AND RANDALL: *Thermodynamics and the Free Energy of Chemical Substances*, p. 282 ff. McGraw-Hill Book Co., Inc., New York (1923).
- (6) Reference 5, pp. 286, 342.
- (7) PARKS AND HUFFMAN: *Free Energies of Some Organic Compounds*, p. 125. American Chemical Society Monograph, No. 60.
- (8) PEARCE AND HICKS: *J. Phys. Chem.* **31**, 231 (1927).
- (9) ROSANOFF AND DUNPHY: *J. Am. Chem. Soc.* **36**, 1411 (1914).
- (10) SAXTON AND SMITH: *J. Am. Chem. Soc.* **54**, 2626 (1932).
- (11) WASHBURN AND READ: *J. Am. Chem. Soc.* **41**, 729 (1919).
- (12) WHITE: *J. Am. Chem. Soc.* **36**, 2292 (1914).
- (13) WILLIAMS AND DANIELS: *J. Am. Chem. Soc.* **46**, 903 (1924).

NOTE TO THE EDITOR

THE OPTICAL ACTIVITY OF CAMPHOR IN ALCOHOLIC SOLUTIONS

In reply to inquiries as to the light source used in the paper of the title given above (Journal of Physical Chemistry **38**, 883 (1934)), Professor Poe states, "All the readings in the paper, 'The Optical Activity of Camphor in Alcoholic Solutions,' appearing in *The Journal of Physical Chemistry*, October, 1934, were made with a Soleil-Ventzke saccharimeter, using white light from an electric light, and filtering it through a solution of potassium dichromate. The scale readings were converted into angular degrees."

NEW BOOKS

The Phenomena of Polymerisation and Condensation. A General Discussion held by the Faraday Society, September, 1935. 25 x 17 cm.; vi + 412 pp. London: Gurney & Jackson, 1936. Price: 22s. 6d.

It may be said without question that this volume is one of the most interesting published by The Faraday Society during recent years. Polymerisation and condensation products are of great fundamental and technical interest and are now receiving due attention. Professor Rideal in his introductory paper distinguishes between three types of polymers: first there are the polymers formed by linear accretion; secondly, those in which a large ring is the structural unit; thirdly, there is the condensation product formed by cross-linkage. The discussion is divided into two parts, called "general" and "special"; each of these contains highly instructive papers. Particular attention should be drawn to the two papers by Staudinger, the first of which is an extremely lucid survey of the formation of polymers of unsaturated substances. Readers coming to the subject freshly would do well to study this paper immediately after Rideal's, in order to gain some idea of the types of product and the relative ease of polymerisation in the various cases.

It is impossible to review individually all of the numerous contributions, but mention may be made of a few of special interest. Already attempts are being made to study the structure of polymers by means of x-rays; the difficulty is of course that most of them are "amorphous". Katz however shows that interesting deductions may be made by comparing the patterns with those of monomeric substances of similar type. Houwink and de Boer are making valiant theoretical attempts to link up the physical properties of polymers with atomic linkage forces, and their papers deserve close attention. Meyer has studied polymerised sulfur and poly-phosphonitrilic chloride by means of their x-ray diffraction patterns, and Melville and Gray give evidence to show that the vapor of red phosphorus is not polymerised but consists of P_2 molecules. The well-known American authorities on hydrous oxides, Weiser and Milligan, conclude that many of these are not polymerised but simply aggregates of microcrystalline particles with strong adsorptive properties. An interesting and promising application of physical methods to organic polymerisation described by Farquharson consists in following the change of magnetic susceptibility during the process.

For reference purposes the usefulness of these volumes would be improved very greatly by the addition of a subject index; the volume will no doubt serve the purpose of a handbook to many and the price is such that full documentation may be reasonably expected. The work of the editorial committee would be minimized in this respect if each author supplied a brief list of the important points dealt with in his paper.

J. T. RANDALL.

Fluorescence Analysis in Ultra-violet Light. By J. A. RADLEY and JULIUS GRANT. 5½ x 8½ in.; xi + 308 pp. 2nd edition. New York: D. Van Nostrand Co.

This second edition, appearing only three years after the publication of the first edition, signifies the interest in fluorescence analysis as also does the fact that over three hundred papers have appeared in this three-year period. The authors pointed

out in their first edition that "if applied with discretion and under standard conditions, fluorescence analysis is a most valuable aid to the scientific worker, especially in routine work or sorting tests, and may usually supplement, though seldom completely replace, ordinary testing or analytical methods." The difficulty is not only that so many things fluoresce, but that the fluorescence is so often changed by the presence of other molecular species, often in very small amounts and perhaps not even suspected as being present. However, fluorescence analysis is becoming a valuable tool in the hands of those skilled in its use and cognizant of its capricious behavior, consequently an authoritative book covering this field fulfills a useful purpose.

The subject matter covered is as follows: PART I. Theory and Technique of Fluorescence Analysis. The titles of the chapters are as follows: I. Theoretical introduction; II. The production of ultra-violet light; III. Filters; IV. The measurement of the intensity of sources of ultra-violet light; V. Methods and technique of fluorescence analysis. PART II. Applications of Fluorescence Analysis. The titles of the chapters are as follows: I. Agriculture; II. Bacteriology; III. Botany; IV. Constructional materials and glass, etc.; V. Drugs; VI. Foods and food products; VII. Fuels and lubricants; VIII. Inorganic chemistry; IX. Leather and tanning; X. Legal and criminological work; XI. Medical and biological science; XII. Minerals and gems; XIII. Museum work; XIV. Organic chemistry; XV. Paints and varnishes; XVI. Paper, cellulose and allied industries; XVII. The rubber industry; XVIII. Textiles; XIX. Waters and sewage.

This is an excellent book, well written and printed, dealing with a subject of much importance and interest. It should be in every chemical library.

J. H. MATHEWS.

Collected Scientific Papers of Sir William Bate Hardy, F. R. S. Published under the auspices of the Colloid Committee of the Faraday Society (preface by Eric Rideal). 17.5 x 26 cm.; xi + 922 pp.; portrait; 14 plates; many figures. Cambridge, England: The University Press (New York: The MacMillan Company), 1936. Price: \$18.00.

It is given to a few men to make a major impression upon the scientific thought of their times. Sir William was one of this chosen few. His contribution was all the more remarkable because of the breadth of his influence. He made major contributions to such diverse fields as zoology, morphology, cytology, physiology, biochemistry, physical chemistry, colloid chemistry, physics, and engineering. His education at Gonville and Caius College, Cambridge, was as a zoologist; following graduation he remained in the laboratories of his college, becoming a Fellow of the College in 1892 and later Demonstrator and then Lecturer in Physiology in the University of Cambridge. During this early period in his educational career (1892-1898) he published eleven papers dealing primarily with the histology, morphology, behavior, and function of the free living or "wandering cells" (i.e., the leucocytes) of crustaceans, amphibians, and mammals. It was this series of studies which led him into the field of surface phenomena. As Rideal notes in the preface of the present volume, Sir William once saw a cell divide under the microscope and he asked himself the question, "Why does a cell divide?" This question motivated Sir William's future work in that borderline field between biochemistry, physics, colloid chemistry, and physiology, and led him to investigate surface and interfacial phenomena.

In 1899 he published two classic papers in the *Journal of Physiology*. One was entitled "On the Structure of Cell Protoplasm"; the other "On the Coagulation of Proteid by Electricity." These were his beginning papers in colloid chemistry. They reflected his earlier interest in cytology, morphology, and histology. In the

histological methods which he had used the tissues were fixed, hardened, dehydrated, and stained for microscopical observations. Sir William questioned whether or not such drastic treatments may not have produced from the complex colloidal matrix of the living cell structures which were in reality artifacts. So his colloid chemical studies began from the necessity of testing such a hypothesis.

Sir William was not fundamentally trained in chemistry, physics, and mathematics, but he acquired the necessary working knowledge of these fields after his formal education had been completed in the University.

His study in 1903 of the effect of the rays from radium on protein sols is one of the earlier papers on the effect of radium rays on biocolloids or living tissues. His studies of the physics and chemistry of the "boundary state" were pioneer studies in that field and early led into problems of adhesion. These problems of adhesion in turn led to his studies on the fundamentals of lubrication and the concept of the orientation of molecules, this concept antedating the later work of Harkins and Langmuir and being arrived at from an entirely different viewpoint.

To Sir William's studies on the equilibrium of the protein in the blood we owe the concept of the isoelectric point as a fundamental and characteristic property of the proteins and other colloid systems.

In the present volume all of Sir William's papers have been brought together and reprinted in chronological order. They comprise fifty-nine papers in number, beginning with a study of the histology and development of the hybroid, *Myriothele phrygia*, in 1891 and ending with the Abraham Flexner lecture "To Remind—A Biological Essay", a philosophical summing up of his life interests (delivered in 1931 but not printed until 1934). Many of the early biological papers are illustrated with plates of careful drawings, beautifully colored. The only criticism of the volume that the reviewer would offer is that it does not contain a biographical sketch. Consequently, the young reader may be left ignorant of the fact that Sir William was first and last a biologist, who used the tools of physics and chemistry to attack a fundamental biological problem.

The world of science is indebted to the Colloid Committee of the Faraday Society for making all these valuable papers accessible in one volume. The reviewer knows of no more inspiring volume to place in the hands of the young student of living processes, be he labeled botanist, zoologist, physiologist, biochemist, or biophysicist. May it assist some of these to carry on the task which Sir William laid for himself; for he says "the biologist's job is to take the findings of physics and chemistry and faithfully to apply them to the riddle of this impossible elusive living slime in its coat of many colors."

ROSS AIKEN GORTNER.

Adsorptionstechnik. By FRANZ KRZIL. 22 x 15.5 cm.; 132 pp. Dresden and Leipzig: Theodor Steinkopff, 1935. Price: 8.50 RM.

For one who knows adsorption mainly from the scientific laboratory it is interesting to see the enormous technical application which has developed, especially in the last twenty years. Solitary cases of technical adsorption processes are very old: the ancients used charcoal or clay to clarify wine; Lowitz in 1785 improved the quality of spirit by letting its vapor pass over charcoal; since 1794 charcoal—later bone-black—has been used in sugar refining. But it was the war and the adsorbent charcoal in the gas-masks which made the many possibilities of adsorption processes generally known.

Active carbon, bleaching clays, kieselguhr, and silica gel are the chief types of adsorbents. They are not only used to remove unwelcome impurities (coloring

matters, etc.) from gases and liquids (drying and desulfurizing of gases; purification of water; refining of glycerol, of oils, resins, etc.). Valuable vapors are regained or isolated by adsorption; explosive gases such as acetylene are stabilized when adsorbed in mixture with acetone; adsorption processes are used in refrigerators.

Krzil's book is clearly and concisely written. It adheres staunchly to its title; stress is mainly laid upon the technical devices used in these processes. Theory is treated very briefly, but correctly. The question which is most important in technical application can not yet be answered from a theoretical point of view; too little is known about the causes of the specific behavior of adsorbents and adsorbed substances.

H. FREUNDLICH.

Lehrbuch der physikalischen Chemie. By K. JELLINEK. Band V, Lieferung 2. 25 x 16 cm.; pp. 289-576. Stuttgart: F. Enke, 1935. Price: 27 RM.

The present section of this well-known work deals with the photoelectric effect, positive rays, the structure of the nucleus, spectra, and radioactivity. The theory of spectra is brought into relation with the Periodic System. The discussion of spectra is based on the Bohr-Sommerfeld theory, and full deductions of mathematical equations, including the necessary analytical geometry, are given. The wave-mechanical treatment is not included. The section on nuclear physics is divided into two parts, the latest results being given separately at the end of the book. The section of spectra also includes x-ray spectra and crystal structure. The whole treatment is very clear, and the average student of physical chemistry would have no difficulty in following the author through some rather difficult parts of the subject. Presumably some account of wave-mechanical methods will be given in a later section dealing with molecule formation. The last few pages deal with the structure of molecules and stereochemistry. The general character of the book is maintained, and the present section is a very readable and intelligible account which should make an appeal to physical chemists.

J. R. PARTINGTON.

Textbook of Quantitative Inorganic Analysis. By I. M. KOLTHOFF and E. B. SANDELL. 5½ x 9 in.; 749 pp.; 116 figures. New York: The Macmillan Company, 1936. Price: \$4.50.

This textbook of quantitative analysis from the hand of such a distinguished contributor in the field of analytical chemistry as Professor Kolthoff, who for many years has also been a successful teacher, is certain to prove immediately attractive to a great many teachers of the subject. The work covered is presented under the following heads: Stoichiometry. Gravimetric Analysis: Theoretical, Practical, Gravimetric Determinations. Volumetric Analysis: Theoretical, Practical, Volumetric Determinations. Physicochemical Methods. Analyses of Complex Materials (Brass, Steel, Silicate Rocks). It concludes with a very brief appendix containing tables of specific gravity of acids and ammonia and a table of four-place logarithms. It will be noticed that the outline above returns to the older practice of giving gravimetric determinations before volumetric.

In the opinion of this reviewer, the most noteworthy feature of the text is the highly successful manner in which theory and practice have been blended together. The sections on the mass action law and its application to strong and weak electrolytes, dissociation of water, hydrolysis of salts, buffer solutions, the solubility product principle, common ion effect, and complex ion formation are particularly lucid. It was to be expected that the chapters on the formation and properties of precipitates and coprecipitation phenomena, covering contamination of precipitates, ad-

sorption, digestion, aging, etc., would be among the strongest in a test by Professor Kolthoff. All that need be said is that these are up to expectation. In addition to the separate sections on these highly important theoretical aspects of quantitative analysis, there occur in the appropriate places throughout the text many applications of these principles to the particular analytical procedures under consideration. On the other hand the authors have laid great stress throughout the procedures on the importance of careful and accurate laboratory technique and the avoidance of experimental errors.

A field to which the senior author has given major attention both in research and as a teacher is that of acid-base indicators, and the section devoted to this subject is admirably done, including an excellent theoretical discussion, many examples of titration curves from experimental data in accompanying tables, a fairly complete table of common indicators with their color change pH interval, methods of preparation of indicator solutions, use of mixed indicators, etc.

The section on physicochemical methods, including potentiometric and conductometric titrations, colorimetry, and spectrophotometry is a welcome addition. Several laboratory procedures on colorimetry, for the determination of ammonia, ferric iron, and silica, with the use of the Duboscq colorimeter, are included. The theory of potentiometric and conductometric titrations is very thoroughly discussed. It is strange that no analytical determinations making use of these methods are outlined, since there are many applications of both these methods which do not involve prohibitively complicated or expensive apparatus. The theory of adsorption indicators is given comprehensive treatment, and several titrations are outlined which make use of this method for obtaining end points.

The authors are apparently quite willing to take the field almost single-handed in defense of the rather nice distinction between the use of the terms "iodimetry" and "iodometry."

The volume is a distinctive addition to the library of quantitative analysis. No instructor in the subject will wish to be without it.

C. H. SCHIFLETT.

Inorganic Chemistry. By N. BJERRUM, translated by R. P. Bell. 22 x 14 cm.; x + 317 pp. London: W. Heinemann, 1936. Price: 7s.6d.

In a foreword to this volume Professor F. G. Donnan states that this book is the finest introduction to modern chemical science that he has read. This is very high praise indeed. It will be generally agreed that no modern textbook dealing with inorganic chemistry can afford to ignore the profound influence exerted by developments in physical chemistry. In the present volume the skillful weaving of the theoretical aspects of inorganic chemistry with the very important descriptive parts of the subject calls for the highest praise, whilst the sections dealing with the modernized theory of acids and bases and the associated subject of ionization and reaction in solution make delightful reading. There is, however, one notable omission from the book. No reference is made to the crystal structure of the mineral silicates. Silicon occupies in mineral chemistry the same important position that carbon holds in organic chemistry, and the structure of the silicates is now as fully established as the molecular structure of any organic compound. Incidentally the model given in this book of the diamond crystal lattice (figure 14, p. 163) does not show the structure to the best advantage. However, whilst these are matters of opinion there can be only one opinion on the book—it is a highly reliable and most stimulating work which will be widely read by chemists. Mr. R. P. Bell has given us a fine translation, which is published in a most attractive form.

W. WARDLAW.

Die Interferenzen von Röntgen und Elektronenstrahlen. By M. VON LAUE. 22 x 15 cm.; 46 pp. Berlin: Julius Springer, 1935. Price: 3.60 RM.

During the autumn of 1935 Professor Laue gave a course of five lectures at Princeton, N. J., and the admirable suggestion of a wider audience has resulted in the production of this small volume. Laue's name will always be associated with that of other pioneers in the subject of x-ray interferences, and it is a matter of some interest that his latest work explains not only a newly observed x-ray diffraction effect, but also the elusive phenomenon of the Kikuchi lines in electron diffraction by single crystals.

The older theory of x-ray interference, as developed by Laue, Darwin, Ewald, and others, was entirely adequate to explain the positions of the diffraction maxima, but failed in certain little-observed respects with regard to intensities. During 1935 a new phenomenon was observed and reported by Kossel and Voges; the x-rays issuing from a single crystal anticathode act as a source of radiation within the crystal, and interference effects are observed on a photographic plate placed parallel to the crystal face. The theoretical work of Laue and Kohler joins up the older classical theory with the quantum theory in order to explain these effects, and the bridge between the two is Maxwell's law of reciprocity. The interesting thing is that the new x-ray patterns are, so far as present results go, entirely similar to the Kikuchi patterns of electron diffraction. Although unexplained details remain, the Kohler-Laue theory work provides a comprehensive theory of these effects. In spite of Professor Laue's mathematical erudition the reprinted lectures are very readable and deserve translation.

J. T. RANDALL.

Veröffentlichungen aus dem Kaiser Wilhelm-Institut für Silikat Forschung in Berlin-Dahlem. Siebenter Band. Edited by W. Eitel. 29 x 21 cm.; 203 pp. Braunschweig: F. Vieweg, 1935.

The annual reproduction in volume form of the published work of the Kaiser Wilhelm-Institut serves two useful purposes; many of the papers appear in somewhat obscure journals and might otherwise be missed. The volume, apart from the individual merits of the papers, is more useful in indicating the trend of fundamental work on silicates in Germany. The present volume contains twenty-five papers, two of which are concerned with problems of Portland cements; another interesting paper by C. A. Becker contains much information on the physical and chemical properties of complicated glasses containing beryllium oxide. The properties of lime-soda-silica glasses containing traces of radium and thorium salts are investigated by M. Heckter, and this is followed by a long study of the system $\text{CaO-SiO}_2\text{-MnO}$ with the x-ray identification of solid solutions of pseudo-wollastonite and rhodonite. Büssem gives x-ray data on the coefficients of thermal expansion for magnesite, cristobalite, sillimanite, and carborundum. The volume closes with a very long paper by W. Weyl, giving details of numerous absorption spectra for solutions and glasses. One gets the impression that the workers on this interesting subject are tending increasingly to use physical methods for the study and interpretation of their experiments.

J. T. RANDALL.

Chemical Discovery and Invention in the Twentieth Century. By SIR WILLIAM A. TILDEN. 492 pp. New York: E. P. Dutton & Co., 1936. Price: \$4.00.

The sixth edition of this meritorious and semi-popular book has been thoroughly revised by Dr. S. Glasstone of the University of Sheffield. In the preface, Glasstone states that the new material has been selected so as to fit in the structure and con-

tinuity of the earlier editions. Obsolete material has been dropped. The additional subject matter includes theories of atomic structure and molecular architecture, valency, transmutation and disintegration of the elements, heavy hydrogen and its theoretical significance, and artificial radioactivity. The new descriptive matter includes among other topics: coal and petroleum industries, synthetic rubber, plastics, fixation of nitrogen, vitamins, hormones, and plant colors.

The book is divided into four parts. I. (a) British laboratories and their uses (this section will always be of historical value). (b) Apparatus. II. Modern discoveries and theories. Clear and non-mathematical. III. Modern applications of chemistry. This includes the more recent work on vitamins, hormones, plastics, rayon, and duprene. IV. Modern progress in organic chemistry.

There are over one hundred and forty illustrations, including a dozen portraits. The author has used discrimination and good judgment in the selection and treatment of his topics. There are one or two noticeable typographical errors. For instance, I. Langmuir is called J. Langmuir (p. 241) and W. S. Harkins is called H. S. Harkins (p. 159).

The reviser states that though the book was intended originally for "non technical" readers, it contains much which would appeal to those who have some knowledge of science. Therefore it is a valuable addition to a chemistry library and can be included as collateral reading for general inorganic chemistry courses.

LILLIAN COHEN.

Molekulspektren und ihre Anwendung auf chemische Probleme. Vol. II, Text. By H. SPONER. 21 x 14 cm.; xii + 506 pp. Berlin: Springer, 1936. Price: unbound, 36 RM.; bound, 37.80 RM.

Volume I (Tables) of this work was reviewed in the December 1935 issue of this Journal. Its high standard of excellence is fully maintained in the present volume. The first two chapters deal briefly with the earlier quantum theory of atomic spectra and the quantum mechanics. Diatomic and polyatomic molecular spectra occupy the third and longest chapter in the book. Certain branches of the subject, however, are omitted and others treated very briefly, either because they have been adequately described in other well-known books of recent years or because they are of comparatively little significance for the chemical problems to which the four remaining chapters are devoted. Chapter IV deals with the determination of chemically important quantities from the analysis of band spectra, chapter V with chemical binding and valency, chapter VI with excitation of molecules by collision with electrons, atoms, molecules, and ions, and chapter VII with other chemical applications of spectroscopic results. The text is well illustrated with 87 figures, including a few spectrograms; figures 15 to 19 (pp. 51 and 54) and figure 43 (p. 118), however, would be much more useful if provided with scales of wave-length or wave-number. A further table of numerical data and a list of references of papers which appeared up to the autumn of 1935 are provided, so that the tables and text are equally up-to-date. The complete work may confidently be recommended to physical chemists and spectroscopists alike.

W. JEVONS.

X-RAY DIFFRACTION STUDIES OF CHITIN, CHITOSAN, AND DERIVATIVES¹

GEORGE L. CLARK AND ALBERT F. SMITH

Department of Chemistry, University of Illinois, Urbana, Illinois

Received June 6, 1936

INTRODUCTION

Chitin is the compound that makes up most of the organic part of the skeletons of *Arthropoda*. In the animal kingdom, to which it is limited with very few exceptions, it occurs only in the invertebrates. In addition to forming the exoskeletons of insects, crustacea, etc., it is the major constituent of the lenses of the eyes, the tendons, and the linings of the respiratory, excretory, and digestive systems. Its rôle in forming the skeleton in invertebrates is very similar to that of cellulose in plants.

When the "encrusting" materials that occur with chitin have been removed, the pure material resembles paper pulp in appearance. Usually calcium carbonate is one of the "encrusting" substances; in the case of lobster skeletons it makes up about 75 per cent of the total weight of the shells. In the tendons, at least, we have found that this material is so finely dispersed that it does not give a crystalline diffraction pattern. The tensile strength of a fiber of chitin is remarkable. Schulze (10) records that it is 58 kg. per square millimeter compared with 35.6 for silk, 14.5 for wool, and only 50 for drawn copper.

Hot saturated sodium hydroxide hydrolyzes chitin slowly, but weaker solutions do not affect it. It is soluble in concentrated mineral acids and anhydrous formic acid, but is unattacked by others.

Meyer and Mark (8) suggested that chitin is identical with cellulose except that the secondary hydroxyl on the alpha carbon atom of the latter is substituted by an acetamide group. This structure received important support when Bergman (1) isolated chitobiose and it is now generally accepted, although Shorigin (12) has recently stated that the unit of the structure is neither glucose or mannose, but another sugar, chitose, differing in configuration. Figure 1 shows the structure proposed by Meyer and Mark compared with that of cellulose.

¹ Presented in part before the Cellulose Division at the Ninety-first Meeting of the American Chemical Society, held in Kansas City, April, 1936. Based on a thesis submitted by Albert F. Smith to the Faculty of the University of Illinois in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1936.

From an excellent fiber pattern obtained from the tendon of *Palinurus vulg.*, Meyer and Pankow (9) found that chitin was orthorhombic and crystallized in space group V_3 or V_2 . They favored the former. Their determination of structure was fairly complete except for the fixing of the side chains. These they assumed to be in the 200 plane to account for its great intensity. The size of the unit cell was $a = 9.25$, $b = 10.46$, and $c = 19.25$ A.U.; the chains are parallel to the b axis. The unit cell is shown in figure 2. Our measurements check those of Meyer and Pankow very closely.

MATERIALS AND TECHNIQUE

Chitin was obtained from the carapace of lobster, *Homarus americanus*. It was prepared by removing the carbonate with dilute nitric acid, heating

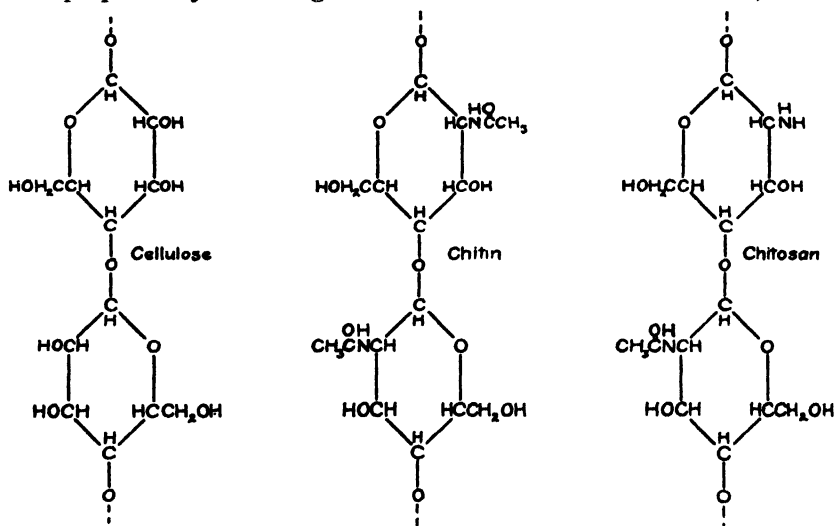


FIG. 1. Structural formulas for cellulose, chitin, and chitosan (as proposed by Löwy)

for four hours with frequently changed 20 per cent sodium hydroxide, bleaching with permanganate and bisulfite, and finally dehydrating with alcohol and ether. The nitrogen content was 6.61 per cent, compared with a theoretical value of 6.89 per cent. The ash was less than 0.1 per cent.

The source of x-rays was a Philips Metalix copper-target commercial diffraction tube operated at 30 kv. and 25 ma., generating principally the Cu K alpha lines. The diffraction patterns were registered on a flat film perpendicular to the beam with the sample 5.0 cm. from the film.

GENERATION AND ORIENTATION OF CHITIN

In view of the great functional and structural similarity of chitin and cellulose, it seemed possible that there might be a similarity in method of generation. Investigation of the literature revealed that Borodin (2)

in a paper little known to chemists, on the slime glands of a marine worm indigenous to northern Europe, had observed tiny ellipsoidal particles that formed in the epithelial cells and were present in the cuticula. Although he apparently did not realize it at the time, his staining reactions leave little room for doubt that he observed the formation of "macromolecules" of chitin several years before similar observations were published on cellulose (4).

In search of further information concerning the structure, we found that after long soaking in absolute alcohol, which seemed to remove a wax-like binding material, a mandibular tendon from lobster could be teased apart with the aid of fine needles into uniform fibrils. These fibrils were about a micron in diameter and between crossed Nicols gave very sharp parallel

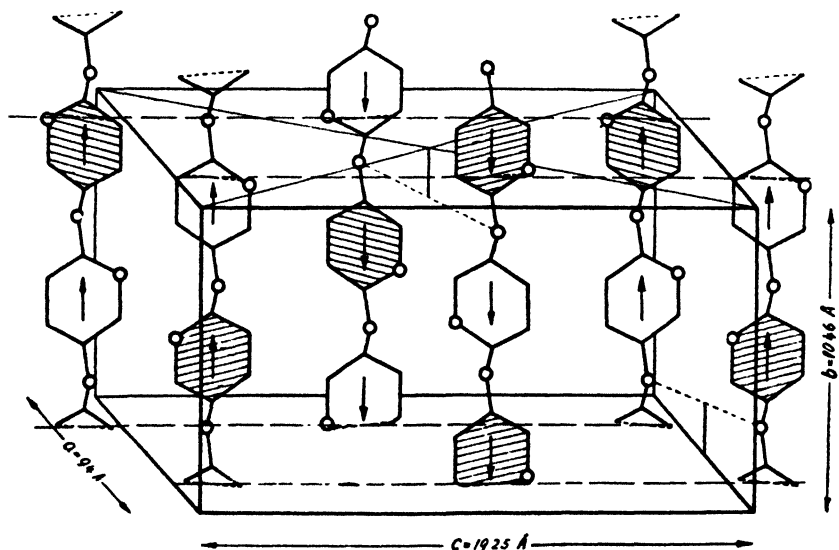


Fig. 2. Unit crystal cell of chitin (Meyer and Pankow, confirmed in present work)

extinction, indicating a high degree of orientation. They seemed to be very similar to fibrils obtained from cellulose. So far we have been unable to break these fibrils down into uniform smaller units, as has been done for cellulose.

From the manner of formation, chitin should be oriented. Further the orientation, in the case of sheets, should consist solely in having the carbohydrate chains parallel to the surface. If this were the case, an x-ray diffraction pattern taken with the beam perpendicular to the surface of the sheet would show the concentric rings of a random pattern. If the pattern were taken with the beam parallel to the surface, however, fibering should appear.

If an orthorhombic crystal, as chitin appears to be, is laid on a surface in

such a way that the b axis is parallel to the surface and the crystal is allowed to rotate about its b axis, and also about an axis perpendicular to the surface, the locus of the face poles of any plane parallel to the b axis, which in chitin amounts to being parallel to the chains, may be represented on spherical projection by lines of longitude. Figure 3 shows the appearance of such a sphere viewed from a pole.

The radial lines represent the lines of longitude. The number of lines per unit area at any point represents the average number of times that the plane is in this position. If a beam of x-rays, x , parallel to and in the plane of the paper, is incident on the rotating crystal, the positions of the plane when satisfying the Bragg angle will be represented on the sphere by a circle or in the projection by the band ab . Since the intensity of any part of an interference on the diffraction pattern depends on the number of times the plane is in the position to give that reflection, and since the lines per

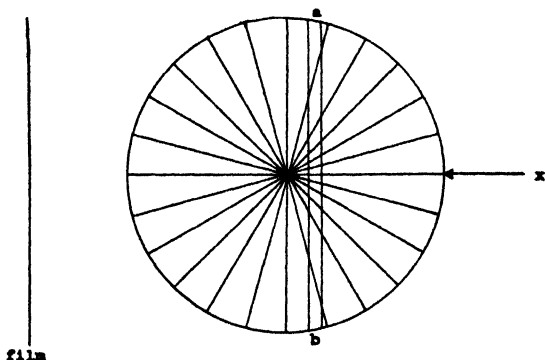


FIG. 3. Spherical projection of intensity distribution for chitin diffraction pattern

unit area in the band ab indicate that number, it is possible to predict the appearance of the diffraction pattern. Since there will always be some lines per unit area in the band, there will appear a continuous ring, but since near the center of the band there occurs a maximum number, there will appear at the equatorial position on the film, the position perpendicular to the plane in which the crystal is rotating, a maximum intensity of the interference.

Any planes perpendicular to the b axis will give obviously only sharp arcs at the polar positions. Planes with inclinations to the b axis other than these will give intermediate appearances. If, in place of a single rotating crystal, there is substituted a large number of very small crystals whose only orientation is the b axis in a plane, the pattern will in no way be altered. Just such a pattern was obtained and is shown in figure 5, which is to be compared with the pattern taken with the beam perpendicular to the surface, figure 4. It was found that all naturally occurring chitin laid

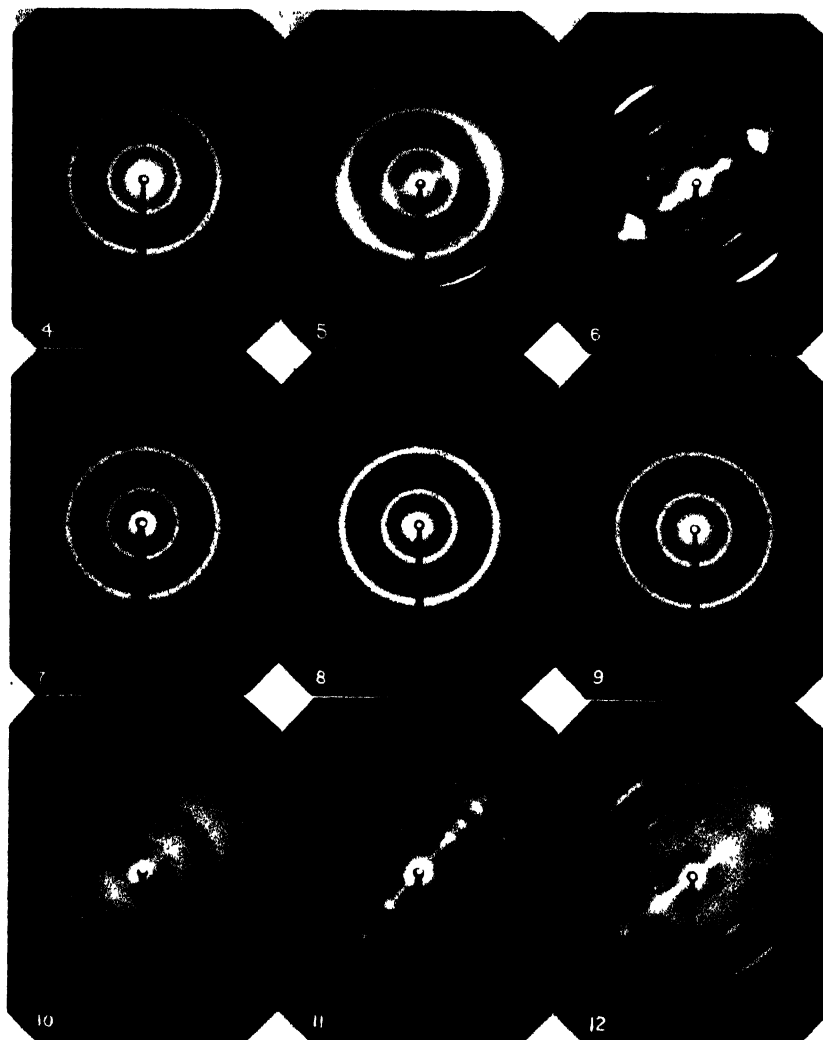


FIG. 4. Chitin sheet, x-ray beam perpendicular to surface.

FIG. 5. Chitin sheet, x-ray beam parallel to surface.

FIG. 6. Chitin fiber (mandibular tendon of lobster).

FIG. 7. Ground chitin.

FIG. 8. Chitin sheet reprecipitated from hydrochloric acid solution after one and one-quarter hours.

FIG. 9. Chitin sheet reprecipitated from hydrochloric acid solution after forty-two hours.

FIG. 10. Chitin sheet reprecipitated from lithium thiocyanate solution.

FIG. 11. Addition compound of chitin with lithium thiocyanate, formed above 200°C.

FIG. 12. Chitin swollen in lithium thiocyanate solution below 200°C.

down in sheets is oriented in this manner. In chitin fibers such as tendons, of course, the b axis is parallel to the axis of the fiber, just as is true in the case of cellulose.

A fiber pattern of chitin obtained from the mandibular tendon of lobster is shown in figure 6. It is entirely similar to the pattern used by Meyer and Pankow in their determination of the crystal structure. The fogging that proceeds outward from the central spot along the equatorial line indicates that parallel to the chains there exist planes of very long spacings. Since it has been possible in the case of some naturally occurring substances, such as collagen (3), to resolve these smudges into definite interferences by swelling, stretching, etc., attempts were made to do the same with chitin, but without success. It is apparent that the diffraction is taking place from planes that are so distorted as to provide a large number of spacings varying only a little in magnitude, resulting in radial smudging of the type so familiar to investigators of distortion in metals.

THE ACTION OF HYDROCHLORIC ACID ON CHITIN

It is well known that boiling concentrated hydrochloric acid eventually hydrolyzes the ether and amide linkages in chitin to give glucosamine, but many workers (6) have believed that in cold hydrochloric acid no hydrolysis occurs and hence have used the reaction to "purify" chitin. Kunike (6) used solution in acid and reprecipitation as a way of obtaining threads of chitin which he hoped to make into fabric, but the venture was not very successful. We have formed a sheet of chitin by reprecipitating it from hydrochloric acid and allowing it to dry on glass. Its tensile strength was so great that it pulled bits of glass out of the surface, but it was readily dispersed in water.

In order to discover the exact nature of the action of the acid, diffraction patterns were taken of chitin reprecipitated after various lengths of time in solution at room temperature. The patterns are shown in figures 8 and 9 along with a pattern of ground chitin for comparison (figure 7). It is necessary to compare with the pattern of a ground sample, since the intensity relationships of the interferences in the pattern taken perpendicular to the surfaces are not quite correct because of the restriction of the orientation.

In these patterns the first heavy line from the center is the interference of the 002 planes, which are parallel to the chains (the b axis) and approximately perpendicular to the plane of the anhydroglucose rings and the side chains. The second heavy line is the interference for the 200 planes, which are parallel to the chains and perpendicular to 002, so that they contain the rings and the side chains. The third heavy line is the combination of the interferences 030 and 031, since their spacings are so nearly the same that their interferences fall at the same point. These planes are

approximately perpendicular to the chains, the 002, and the 200 planes. This applies to all of the other patterns shown in this paper. Since the intensity of a given interference depends upon the number of planes giving the reflection, any action that destroys the regularity of spacing in a given crystallographic direction will reduce the intensity of interferences from planes perpendicular or nearly perpendicular to this direction.

In the pattern of the material precipitated after one and one-quarter hours in hydrochloric acid solution (figure 8), the intensity of the interference 030, 031 is appreciably less than in the pattern of the ground chitin (figure 7). In the pattern of the material reprecipitated after 42 hours (figure 9), the intensity has decreased until the line can hardly be designated as strong. In addition to the decrease in intensity, there is a considerable broadening which indicates that the particle size in the direction of the *b* axis, that is, along the length of the chains, has been considerably reduced. The decrease in intensity indicates plainly that there has been a reduction in the length of the chains with the consequent destruction of the 030 and 031 planes. This must mean that there is occurring, even in the cold solution, a hydrolysis of the ether linkages between the anhydroglucose units. A pattern taken of material precipitated after five days in the acid shows further decrease in the intensity of the 030, 031 interference and in addition a reduction in intensity of 002. This last must result from the hydrolysis of part of the acetyl groups in the chain, causing some of the chains to draw closer together in the *c* direction, thus destroying the regularity necessary for diffraction to take place. That the 200 interference should exhibit the same intensity throughout the series is to be expected, since there is no action occurring to alter that spacing. All patterns were taken under the same conditions to permit comparison of intensities.

Since it is apparent that appreciable reduction of the chain length occurs in so short a time as one and one-quarter hours, it seems possible that Kunike's lack of success in making a satisfactory fabric may be explained on that basis. The ready dispersion of the chitin sheet formed from reprecipitated chitin and the increased difficulty of precipitation with longer time in solution is explained by greater solubility which accompanies a decrease in chain length. The generation of a few amine groups by the slow hydrolysis of the amide linkage, which is shown to occur, would also contribute toward greater solubility.

The purification of chitin by solution in hydrochloric acid and reprecipitation is obviously unsatisfactory.

Although chitin dissolves rather sharply in hydrochloric acid when the normality reaches 8.5, in sulfuric acid the normality must be considerably higher, and concentrated nitric acid has practically no effect. Apparently the solubility does not depend upon the hydrogen-ion concentration alone.

THE ACTION OF LITHIUM THIOCYANATE ON CHITIN

It has been known for some time (13) that chitin and a number of other highly polymerized substances are dispersed in hot concentrated solutions of neutral salts capable of a high degree of hydration, and that they may be reprecipitated in the form of filaments when these salt dispersions are poured into alcohol. It seemed worthwhile to investigate the process of dispersion of chitin in lithium thiocyanate.

The lithium thiocyanate solution used was saturated at about 60°C. and solidified upon cooling to room temperature. Upon heating in this solution to 95°C., chitin was rather readily dispersed into a sirupy colloidal solution.

As a precipitating medium acetone in water was found to be superior to alcohol, since the speed of the precipitation could be varied between wide limits by merely changing the proportion of acetone. By extrusion of the solution through a fine tip into a high concentration of acetone in water, threads could be made. When some tension was applied to the threads during their formation, they developed a considerable degree of orientation, as shown by their sharp parallel extinction between crossed Nicols.

Some of the jelly-like mass of chitin precipitated from the colloidal solution by dilution was placed upon a glass surface and allowed to dry. Figure 10 is the diffraction pattern obtained with the beam parallel to the surface of the sheet. It shows to a lesser degree the same type of orientation as the natural sheet. The diffraction pattern of chitin precipitated after remaining for several months in lithium thiocyanate showed no evidence of any hydrolysis.

Lithium iodide acts in the same way as lithium thiocyanate, but more slowly.

When a chitin fiber was heated to 200°C. in the lithium thiocyanate solution, we found that although there was little change in volume and the form remained the same, the diffraction pattern, figure 11, showed definite compound formation with the salt. Accurate chemical analysis was impossible, since any attempt to remove the excess salt by other than mechanical means results in destruction of the compound, but such results as were obtained showed some value less than 5 moles of lithium thiocyanate per anhydroglucose unit. This addition compound is comparable to the lithium thiocyanate-cellulose addition compounds and, as in the case of cellulose, its formation may be attributed to the ether and alcohol groups. Upon washing in water the salt is removed from the fiber, and the original chitin reappears as well oriented as originally. The interferences of the fiber pattern of the compound are given in table 1, but the determination of the crystal structure must serve as the subject of another investigation.

At temperatures below that necessary for compound formation, a fiber of chitin soaked in the lithium thiocyanate solution gives the pattern shown

in figure 12. Here there is no evidence of compound formation. The interferences of planes parallel to the chains merely become smudged, showing that the regularity of their spacing is being destroyed. The interferences of planes perpendicular to the chains, 030, 031, remain sharp, indicating that the effect of the salt is to spread the chains apart without breaking them and without producing any displacement in the direction of the *b* axis. It is an example of intramolecular swelling of chitin by water alone, also proved by the diffraction pattern. If chitin is allowed to remain in the salt solution sufficiently long, the chains are spread so far apart that solution occurs.

CHITIN NITRATE

In 1906 it was established by Furth and Scholl (5) that chitin could be nitrated with fuming nitric acid to give a substance partially soluble in

TABLE 1

Interferences of the addition compound of chitin with lithium thiocyanate

LAYER LINE	INTENSITY*	d IN A.U.	LAYER LINE	INTENSITY*	d IN A.U.
0	4	7 30	1	1—	3 0
0	1—	6 12	2	1+	5 17
0	2	5 3	2	2	4 48
0	1—	4 46	2	1+	4 19
0	3	4 08	2	1—	3 77
0	1	3 6	2	1—	3 47
0	1—	3 14	2	1—	3 19
1	? 1—	4 56	3	5	3 39
1	1—	3 81	3	1—	3 24
1	1—	3 38			

* An intensity of 5 indicates the greatest intensity on the pattern.

acetic acid. Shorigin and Hait (11) reinvestigated the substance in 1935 and found substantially the same result, but added that a considerable portion was soluble in formic acid. Since the nitrogen content of the fractions was the same, they considered that the difference in solubility arose from some other cause, probably difference in chain length.

For structural studies of nitrated chitin, we prepared specimens by dissolving chitin in fuming nitric acid, allowing it to remain for one or two hours, and precipitating by stirring into water. Since the nitration of each hydroxyl group in chitin would result in an increase in weight of 20.9 per cent, the increase in weight ought to be a satisfactory way of estimating the degree of nitration, but such was not found to be the case. From the increase of weight in one experiment it was calculated that there should be 0.72 nitrate group per anhydroglucose unit, but analysis showed 1.09. The discrepancy may arise from either, or both, of two causes. Nitrogen

may enter in some form other than that of the nitrate, or there may be hydrolysis or oxidation of chitin to some products that were not isolated.

The diffraction pattern of the freshly precipitated material was usually that shown in figure 13. This is a typical "amorphous" pattern, and in this case arises from the very intimate mixing of a large number of different substances with little regularity of structure. Occasionally, especially for very slow precipitation, there was obtained the pattern shown in figure 14. This pattern resembles closely that given by many resins in which the interferences are attributed to side spacings between the chains, and there is no reason to doubt that they arise from the same source in this case. The position of the rings varies from sample to sample and apparently depends on the amount of reaction that has occurred.

Chitin nitrate shows about the same solubility in hydrochloric acid as the original chitin, so that it is unlikely that any considerable hydrolysis of the acetyl groups has occurred. In hydrochloric acid solution there is considerable denitration, and the diffraction pattern of the reprecipitated material shows the pattern of the nitrate superimposed on the pattern of chitin. Chitin nitrate can be dispersed in lithium thiocyanate solution and reprecipitated unchanged.

A typical diffraction pattern of the nitrate fraction soluble in acetic acid is shown in figure 15; actually the pattern varies for every sample and even for different portions of the same sample, demonstrating quite clearly that the material is, as other workers suspected, a mixture of short-chain substances resulting from the hydrolytic and oxidative action of the nitric acid. Its solubility does not arise from hydrolysis of acidamido groups to amine, since it is practically insoluble in dilute mineral acids. A considerable portion of this fraction is soluble in acetone.

The pattern of the fraction insoluble in acetic acid but soluble in formic acid is shown in figure 16. It is more readily duplicated than in the preceding case, so that the admixed substances are apparently in fairly constant proportions. The fraction is unquestionably a mixture of compounds.

The fraction insoluble in formic acid gives a definite pattern (figure 17) and must approach the composition of a pure substance.

In order to determine what alteration had been made in the structure to account for the difference in solubility of the fractions, samples were denitrated by means of aqueous sodium hydrogen sulfide (11). The pattern of the denitrated formic acid-soluble fraction is shown in figure 18. The interference 030, 031 is almost entirely missing, showing definitely that the length of the chain fragments is very short. That there should be hydrolysis of the ether linkages is in harmony with the action of hydrochloric acid observed earlier. In the pattern of the denitrated insoluble fraction (figure 19), the interference 030, 031 has decreased somewhat in

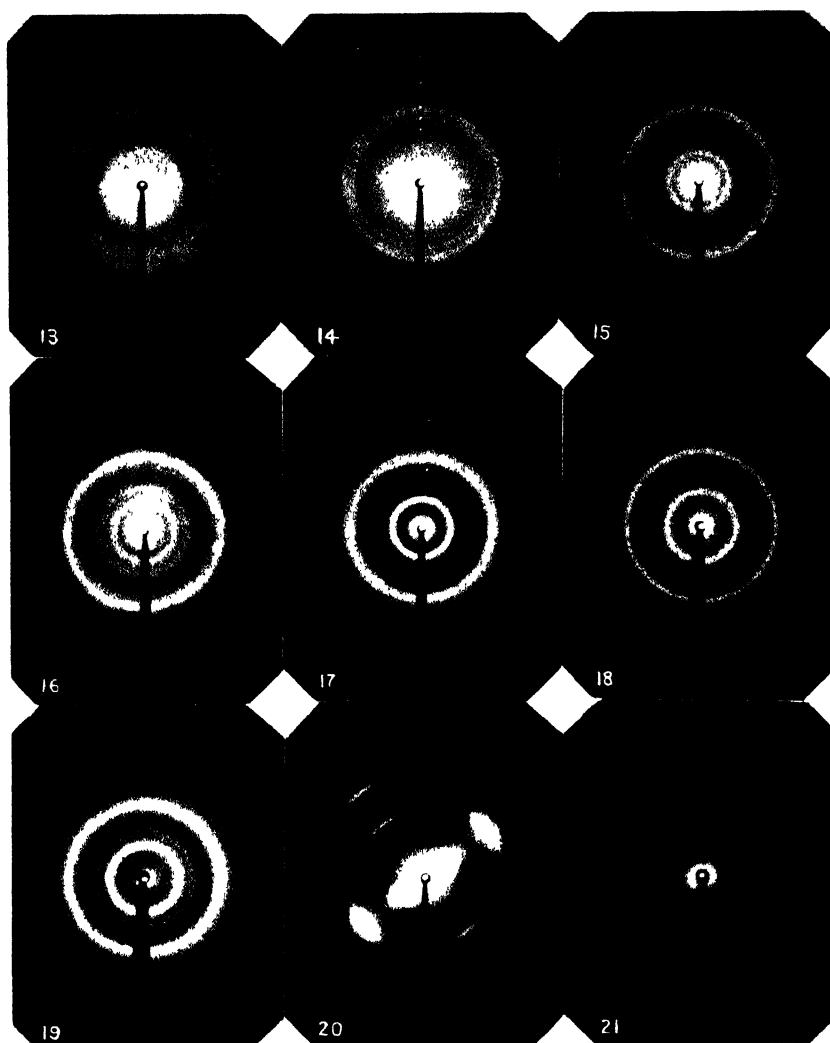


FIG 13 Chitin nitrate freshly precipitated

FIG 14 Chitin nitrate very slowly precipitated

FIG 15 Chitin nitrate fraction soluble in acetic acid

FIG 16 Chitin nitrate fraction insoluble in acetic acid but soluble in formic acid

FIG 17 Chitin nitrate fraction insoluble in formic acid

FIG 18 Specimen of figure 16 denitrated

FIG 19 Specimen of figure 17 denitrated

FIG 20 Nitrated chitin fiber

FIG 21 Addition compound of chitin with sodium hydroxide

intensity from that shown by the original chitin, but it is much stronger than that shown in figure 18. The chain length has been reduced from that in chitin, but to a lesser extent.

When the denitration was incomplete, the pattern of the fraction was always observed superimposed upon the pattern of the chitin. This enabled accurate measurements of the differences in the two patterns. Since the other two fractions are definitely mixtures, the measurements of the interferences observed in the case of the insoluble nitrate only are given in table 2.

Since a fiber pattern was necessary for a satisfactory approach to the analysis of the crystal structure of the nitrate, attempts were made to orient the nitrate, but none were sufficiently successful. We then attempted to nitrate a fiber of chitin without changing its orientation or physical form. This presented difficulty, since acid strong enough to nitrate the chitin also dissolved it. After many attempts the fiber whose pattern is shown in

TABLE 2
Interferences observed in the case of the insoluble nitrate

SOLUBLE FRACTION		INSOLUBLE FRACTION	
<i>d</i>	Intensity	<i>d</i>	Intensity
11 5	4	11 5	5
7 43	3	5 89	1+
5 36	1	5.17-4 53	4
4 9	1-	3 9	1
4 48	5	3 3	3+
3 8	1	2 96	1-
3 3	3	2 6	1

figure 20 was obtained. Nitration was accomplished by using a mixture of 5 parts fuming nitric acid (sp. gr. 1.5) and 1 part of concentrated nitric acid. The action was observed under the microscope so that it could be stopped in time to prevent solution. The fiber was extracted with formic acid to remove the short-chain fractions.

The indistinctness of all interferences except those along the chain shows the incompleteness of the nitration and the correspondingly imperfect crystal structure. That considerable nitration has taken place, however, is shown by the fact that the inner equatorial spacing, 002, has moved into the position shown in the powder patterns of the nitrate.

Chitin nitrate is probably orthorhombic with $a = 9$, $b = 10.3$, and $c = 23$ A.U. The fact that the c distance has increased from the c of chitin indicates that the side-chain primary hydroxyl group does lie in the 200 plane, since the increase is just about what would be expected from the substitution of a hydroxyl by a nitrate group.

THE ACTION OF SATURATED SODIUM HYDROXIDE ON CHITIN

When a fiber of chitin was placed in hot saturated sodium hydroxide, it was found that a series of compounds was formed. A typical pattern is shown in figure 21. The patterns regularly showed definite interferences, but they were difficult to duplicate. The probable explanation is that since hydrolysis is occurring and since, as was later found, chitosan is extremely susceptible to the formation of addition compounds, most of the patterns are of mixtures of several different addition compounds formed in the course of hydrolysis.

CHITOSAN

Most authors have formed chitosan by the action on chitin of fused potassium hydroxide at 180°C. for half an hour, with resultant hydrolysis of half of the acetyl groups. Apparently identical is the product obtained upon long hydrolysis in saturated sodium hydroxide solution, since both give the same diffraction pattern and the same analysis. Lowy (7) found by an analysis of the sulfate of chitosan that it corresponded to a polymerized monoacetylglucosamine. This structure is shown in figure 1.

To follow the formation of chitosan a sheet of chitin was placed in a saturated sodium hydroxide solution held at 95°C. At intervals samples were taken out, washed free of alkali, and a diffraction pattern made with the beam perpendicular to the surface. A specimen removed after treatment for six hours produced a pattern in which interferences characteristic of chitin had disappeared except for the interference 200 which had shifted slightly but still remained (figure 22). This indicates that action occurs to destroy the regularity of spacing in the *c* direction, since it was logical to suppose that the same orientation of the chains would be maintained as long as the sample had not gone into solution. When a powder pattern (figure 23) was taken, however, it became apparent that there was some orientation greater than that exhibited by the original chitin. A pattern with the beam parallel to the surface (figure 24) confirmed the conclusion.

In order to explain these patterns satisfactorily, it was necessary to determine the crystal structure of chitosan. When a fiber of chitin was allowed to remain in hot saturated sodium hydroxide for forty hours to insure complete conversion to chitosan, and the alkali removed by washing, the fiber gave the diffraction pattern shown in figure 25. It displays a remarkable resemblance to the pattern of mercerized cellulose.

Using a mechanical apparatus which we designed for the determination of unit cell size from a single rotation pattern, we found that chitosan was orthorhombic with $a = 8.9$, $b = 10.25$, and $c = 17.0$ A.U.² The chains and the rings lie in the 200 planes. A description of the apparatus and the

² A monoclinic structure with $\beta = 88^\circ$ is not excluded as an alternative possibility.

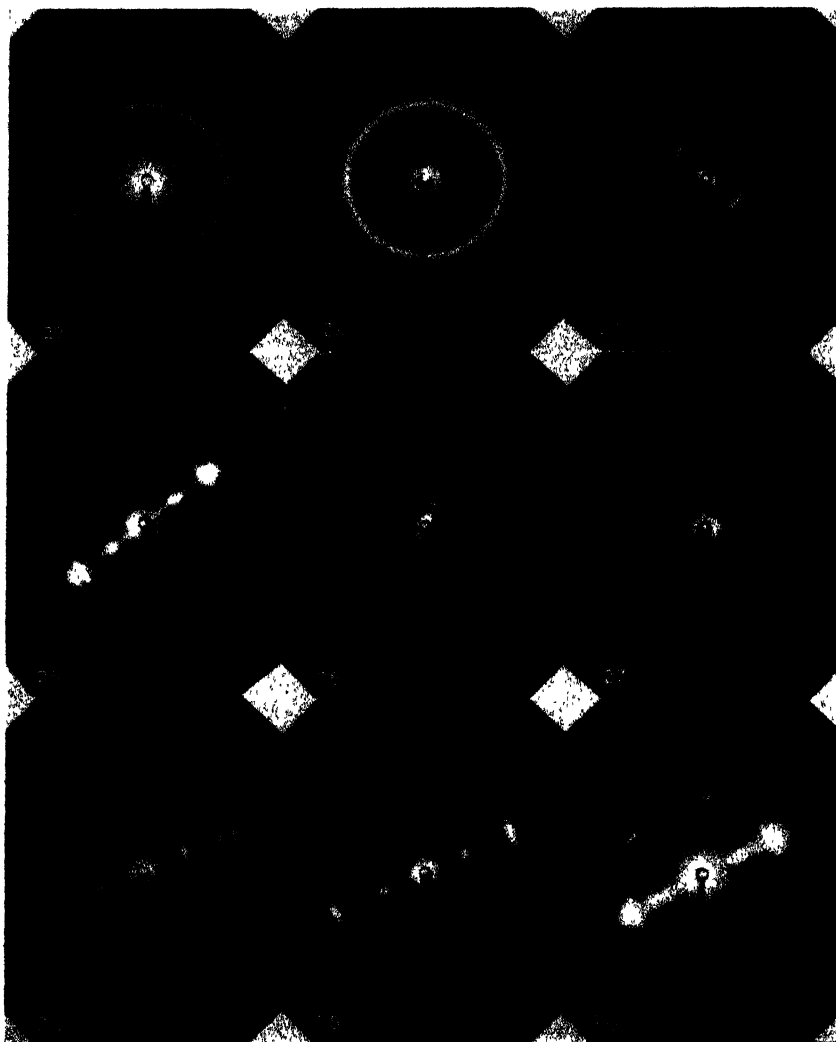


FIG. 22. Chitin after treatment with saturated sodium hydroxide solution for six hours.

FIG. 23. Chitosan sheet, x-ray beam perpendicular to surface.

FIG. 24. Chitosan sheet, x-ray beam parallel to surface.

FIG. 25. Chitosan fiber.

FIGS. 26 AND 27. Addition compounds of chitosan with sodium hydroxide.

FIGS. 28, 29, AND 30. Addition compounds of chitosan with lithium thiocyanate.

details of the crystal structure will be given in a later paper, but the spacings of the interferences, observed and calculated, are given in table 3.

From the crystal structure the orientation existing in the sheet can be deduced. In the pattern taken with the beam parallel to the surface it is

seen that the interferences of planes 002 and 200 do not fall on the equatorial line, but that 002 falls on the equator while 200 occurs at the poles. Since both of these planes are parallel to the b axis, as shown by the fiber pattern, the only possible orientation to account for the diffraction pattern is that 002 planes must be approximately parallel to the surface. A slight variation from parallel of only a few degrees will satisfy the Bragg angle and account for the appearance of the 002 interference on figure 24. This

TABLE 3
Interferences obtained with chitosan

LAYER LINE	hkl	d ORTHORHOMBIC	INTENSITY	OBSERVED
0	002	8.5	4	8.5
0	200	4.45	5	4.46
0	202	3.94	3	4.0
0	203	3.53	1—	3.56
0	105	3.16	1—	3.12
0	006	2.83	1—	2.83
1	211	3.97	1	4.02
1	015	3.22	1—	3.25
1	310	2.84	1—	2.81
2	020	5.12	1—	5.13
2	121	4.31	3	4.35
2	123	3.5	2 (Diffuse)	3.6
2	223	2.90	1—	2.91
2	025	2.84	1—	2.78
3	130	3.20	2	3.23
3	132	3.00	3	3.02
3	230	2.71	1	2.72
4	040	2.56	1	2.50

pattern is excellent confirmation of the orthorhombic structure, since the only possible angle between these planes is 90° if the interferences are to be explained.

Upon taking patterns of the chitosan fiber in a vacuum camera (3) at 15 cm. it was found that *three orders of a long spacing* of 37.5 A.U. occur; on a few patterns there was barely discernible an interference for 25 A.U., which would seem to indicate that the interferences observed were the second, third, fourth, and sixth order of a 75 A.U. spacing. These occur on the equatorial line. Their probable significance will be discussed in the paper on the crystal structure of chitosan.

ADDITION COMPOUNDS OF CHITOSAN

Chitosan is particularly susceptible to the formation of addition compounds. When a fiber soaked in concentrated sodium hydroxide was placed in a "pliofilm" cell, it gave the diffraction pattern shown in figure

26. A fiber soaked in dilute sodium hydroxide (20 per cent) gave the pattern in figure 27. Both of these patterns are of mixtures, and it is likely that chitosan forms a whole series of compounds similar to the sodium hydroxide addition compounds of cellulose. The pattern of the compound with dilute alkali is especially interesting, since in it the long spacings observed in chitosan have moved from 37.5 to 43.5 A.U., presumably to allow for the volume of the swelling agent.

With the lithium thiocyanate solution used in the work on chitin, chitosan gave a material whose pattern is shown in figure 28. If a solution diluted with two volumes of water was used, the pattern shown in figure 29 was obtained. Upon washing either of these fibers, the material giving the pattern in figure 30 was obtained. Upon further washing the original chitosan was obtained. These patterns are fairly readily duplicated, but it is possible that they are not of the pure compounds. These addition compounds of chitosan merit further investigation.

COMMENTS ON THE STRUCTURE OF CHITOSAN

Our analyses of chitosan prepared by either method have indicated only a little more than one nitrogen per biose unit instead of the two demanded by the formula of Löwy (figure 1). Since the amide linkage still exists, as shown by the presence of acetyl, the amine nitrogen appears to have been partly lost. It seems possible that Löwy's work was done on only the portion of the material retaining the amine group, since that fraction alone should form a salt.

Since the chemical information at hand reveals no reason for the hydrolysis of only one-half of the acetyl groups, and since the reaction takes place in the solid, it seems probable that there is steric hindrance to the reaction from *another* molecule. This idea is supported by the fact that since the unit along the chain is two anhydroglucose units, the acetyl groups hydrolyzed all occur on the same side of the chain.

These problems must be further investigated.

SUMMARY

1. All naturally occurring chitin displays preferred orientation of crystallites. The pattern obtained with the x-ray beam parallel to the surface of the sheet of chitin in which the chitin chains are parallel to the surface as the only orientation is derived from a consideration of the spherical projection of a rotating orthorhombic crystal.

2. Naturally occurring fibers of chitin, after treatment with absolute alcohol, may be teased apart into uniform fibrils about 1 micron in diameter.

3. Even at room temperature the ether linkages of chitin are hydrolyzed

in hydrochloric acid; concurrently, but more slowly, the amide groups also are hydrolyzed.

4. A fiber pattern of chitin is shown and discussed. Our measurements check those of Meyer and Pankow very closely.

5. At a temperature of 200°C. chitin forms a definite addition compound with lithium thiocyanate. At lower temperatures, intramolecular swelling occurs.

6. The fractions of chitin nitrate have different average lengths of the carbohydrate chain. Chitin nitrate is probably orthorhombic with $a = 9.2$, $b = 10.3$, and $c = 23$ A.U.

7. Chitin seems to form a series of addition compounds with sodium hydroxide, but the hydrolysis that occurs makes the isolation of definite compounds difficult.

8. When chitosan is formed from chitin in a sheet, it undergoes a change to a more restricted orientation. The 002 planes become parallel to the surface of the sheet.

9. Using an apparatus designed for the determination of unit cell size from a single rotation pattern, the unit cell of chitosan was determined to be orthorhombic with $a = 8.9$, $b = 10.25$, and $c = 17.0$ A.U. (or possibly monoclinic with $\beta = 88^\circ$). A table of interferences and the indices is given, but the details of the determination and a description of the apparatus will appear in another paper.

10. Patterns are given for several addition compounds of chitosan with lithium thiocyanate and sodium hydroxide.

11. It is reported that analyses show only about one-half of the nitrogen required for Löwy's structure of chitosan, and it is suggested that there may be hydrolysis of the amine group to hydroxyl.

12. It is suggested that steric hindrance from an *adjoining* molecule may account for the hydrolysis of only half of the amide groups in chitin by alkali.

REFERENCES

- (1) BERGMAN, ZERVAS, AND SILBERKWEIT: Ber. **64**, 2436 (1931).
- (2) BORODIN: Z. Morphol. Ökol. Tiere **7**, 26 (1929).
- (3) CLARK AND SCHAAD: J. Am. Chem. Soc. **57**, 1509 (1935).
- (4) FARR AND ECKERSON: Contrib. Boyce Thompson Inst. **6**, (2), 189-203 (1934).
- (5) FURTH AND SCHOLL: Beitr. Chem. Physiol. **10**, 188-98 (1907).
- (6) KUNIKE: Kunstseide **8**, 182-3; Chem. Zentr. **97**, II, 2129 (1926).
- (7) LÖWY: Biochem. Z. **23**, 47-60 (1910).
- (8) MEYER AND MARK: Ber. **61**, 1936 (1928).
- (9) MEYER AND PANKOW: Helv. Chim. Acta **18**, 589 (1935).
- (10) SCHULZE: Ent. Mitt. **15**, 420-3 (1926).
- (11) SHORIGIN AND HAIT: Ber. **68**, 965 (1935).
- (12) SHORIGIN AND MAKOROWA-SEMLJANSKAJA: Ber. **68**, 965 (1935).
- (13) VON WEIMARN: Ind. Eng. Chem. **19**, 109-10 (1927).
- (14) WESTER: Arch. Pharm. **247**, 292 (1909).

ALTERATION OF THE FREE SURFACE ENERGY OF SOLIDS. I

VERTICAL-ROD METHOD FOR THE MEASUREMENT OF CONTACT ANGLES AND PRELIMINARY STUDY OF EFFECT OF HEAT TREATMENT ON MAGNITUDE OF CONTACT ANGLES

F. E. BARTELL, J. L. CULBERTSON, AND MIKE A. MILLER

Department of Chemistry, University of Michigan, Ann Arbor, Michigan

Received May 23, 1936

The angle of contact formed between solid, liquid, and gas, or between solid, liquid, and liquid is a function of the tensions existing between the phases in contact. Since the surface tension of a phase is numerically equal to its free surface energy, measurement of contact angles is of importance in connection with studies of free surface energy relations of given systems. Various methods have been employed for measuring the contact angle, as for example, the sessile-drop method, transparent-capillary-tube method, tilting-plate method, rotating-cylinder method, bubble method, drop-on-horizontal-plate method, combination drop-volume and capillary-ascension method, pressure-of-displacement method, and others. Any one of these methods will give reliable results provided it is used under properly controlled conditions. It is of greatest importance that the exact treatment history of the solid phase be known. Failure of different investigators to use solids with the same treatment history accounts largely for the divergent values for contact angles found in the literature.

It became desirable in connection with our researches to adopt some method with which measurements could be carried out rapidly. Preliminary tests indicated that readily duplicable results could be obtained by immersing the solid, in the form of a rod, vertically through a horizontal liquid interface. Other investigators had used a vertical-rod method (4, 7) or a vertical-plate method (2, 3) in investigations dealing with surface energy relations, but no simple rod method had been described which gave readily duplicable results for solid-liquid-air angles and for all types of solid-water-organic liquid interfacial angles. Such a method was developed and has been used throughout this investigation. This method will be referred to as the "vertical-rod" method.

VERTICAL-ROD METHOD FOR OBSERVING SOLID-LIQUID-AIR CONTACT ANGLES

For the measurement of solid-liquid-air contact angles the solid rod was placed vertically through the liquid surface, and a microscope in a horizontal position was focused on the system with the line of contact of the liquid with the solid approximately in the center of the field. In order to secure a true representation of the configuration of the surfaces in such a system, it was necessary that any liquid or solid through which the illuminating light ray was passed be bounded by plane surfaces and be of uniform thickness. For the case of solid-liquid-air systems in which the contact angle was less than 90° it was easy to arrange the apparatus so that observation could be made without having the light ray pass through any liquid or solid media. This was accomplished by filling to the brim with the liquid to be investigated a small rectangular glass cell having one horizontal dimension of approximately 1 cm. (figure 1a). The cell was mounted against the microscope stage and was adjusted so the surface of the liquid appeared in the field of the microscope unobstructed by the sides of the cell. The liquid surface under these circumstances was unprotected

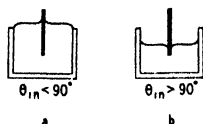


FIG. 1. Cell used for observing solid-liquid-air contact angles

from atmospheric contamination, and it was found best to enclose this small cell in a larger rectangular cell which could be covered except for the small aperture through which the rod was inserted. The large cell had walls of clear plane polished glass.

In case the solid-liquid-air angle, θ_{ln} , was greater than 90° and there was a depressing of the liquid around the rod, the light beam had to pass through the liquid. For this case the cell was but partially filled with the liquid (figure 1b). The illuminating beam of light passed through the cell walls and through the body of the liquid. Since the cell walls were plane and were parallel to each other there was no distortion of the image in the microscope.

VERTICAL-ROD METHOD FOR OBSERVING SOLID-LIQUID-LIQUID CONTACT ANGLES

The arrangement of apparatus used for interfacial solid-liquid-liquid systems depended upon the characteristics of the system under investigation. When water and an organic liquid (immiscible with water) were poured into the cell and a rod inserted, a contact angle solid(rod)-water-organic liquid, θ_{ns} , represented in figure 2, a, b, c, or d, was formed. An-

other contact angle, solid(cell wall)–water–organic liquid, was also formed. Since the cell walls were of glass, they were more readily wetted by water than by organic liquid and the interfacial contact angle of the liquids with the cell wall, when measured through the water phase, was acute. The interfacial angle solid(rod)–water–organic liquid, θ_{n3} , could readily be viewed through a microscope in a horizontal position at the side of the cell in cases a and b, but in cases c and d the interfacial angle solid(cell wall)–water–organic liquid obscured the view. In such cases devices such as are shown in figure 2, c' and d', were utilized. In the diagrams *n* refers to organic liquid, 3 refers to water, the symbol θ_{n3} represents the solid(rod)–water–organic liquid angle which is expressed as measured through the water phase, and symbols d_n and d_3 represent the densities of organic liquid and water, respectively.

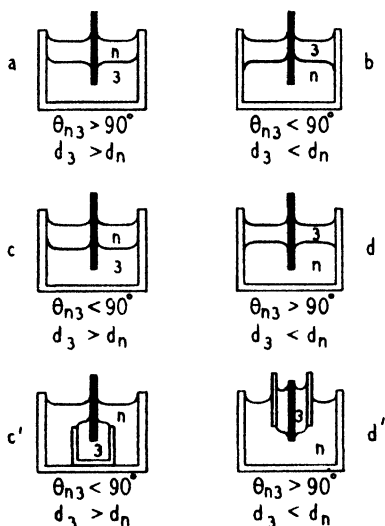


FIG. 2. Cell used for observing solid-liquid-liquid contact angles

Situation c was realized with a silica-water-benzene system. Proper conditions were attained in this case by filling the small (inner) cell to the brim with the denser liquid, and allowing the lighter liquid to flow into the larger cell until the small cell was completely submerged. This gave a liquid-liquid interface at the top of the small cell which was slightly convex upwards. When the rod was thrust vertically through the interface, the angle of contact of the interface on the solid being acute with respect to the denser liquid, the interface rose slightly and was easily brought into the field of the microscope.

Situation d was realized with a silica-water- α -bromonaphthalene system. To obtain an unobstructed view of this system a glass tube, open

at both ends, was supported vertically in the larger cell, with the lower end of the tube at least a centimeter from the bottom of the cell. The lower end of this tube was ground flat, normal to its axis. The tube was about 5 cm. in length and had an inside diameter such that when the solid rod, on which the measurement was to be made, was fixed in its center there was 3 mm. or more of clear space between the rod and the inside wall of the tube. The denser of the two liquids was first run into the cell until the lower end of the open tube was completely submerged. Then by adding the lighter liquid at the top of the open tube, the liquid-liquid interface was pushed down the tube by hydrostatic pressure until it became visible at the lower end of the tube. The solid rod on which measurements were to be made was placed in the center of the tube and was then extended through the liquid-liquid interface. The interfacial contact angle thus formed was easily observed and photographed.

Method of measuring angles

The system to be examined was carefully adjusted; light from an arc was focused upon the rod so as to give good illumination of the line of contact. A microscope in a horizontal position was focused upon the points of contact at the maximum observable diameter of the rod, and photomicrographs were taken. The angles were either measured directly upon the photographic plate (lantern slide size) by means of a specially designed tangent-meter or were measured from the image projected upon a screen.

PRELIMINARY EXPERIMENTS ON EFFECT OF HEAT TREATMENT ON MAGNITUDE OF CONTACT ANGLES

Pyrex and silica rods 1 to 3 mm. in diameter were cleaned by treating with dilute nitric acid, washing with a large quantity of water, steaming, and heating to 450°C. in air for three hours. When these rods were cooled very slowly, they exhibited zero solid-water-air contact angles. When they were cooled rapidly, they gave small finite contact angles with water. Cleaned rods, 3 mm. in diameter, were drawn out to less than 1 mm. by heating either in a blast flame or in a platinum resistance coil. The solid-water-air contact angle varied from a value of zero on the 3-mm. and 1-mm. portions, i.e., maximal and minimal diameters, respectively, to over 30° on the conical section of the rod.¹ Upon examination of the conical section in polarized light, an intense strain was revealed.

Pyrex-organic liquid-air and pyrex-water-organic liquid contact angles were also investigated with such drawn-out rods, but quantitative correla-

¹ A similar observation was made in this laboratory by Bartell and Stenzel who observed finite Pyrex-water-benzene contact angles within cone-shaped capillary tubes (unpublished observation).

tion of the free surface energy changes was impossible because of the impossibility of exactly duplicating a stressed specimen.

Freshly fused, rapidly cooled, solid Pyrex spheres of several millimeters diameter also showed an intense strain when examined between crossed Nicols. Such spheres gave an angle of about 80° with water. It has been suggested that tangential surface stresses exist upon rapidly cooled solid glass spheres (8). Removal of the strain by careful annealing caused the spheres to give zero solid-water-air contact angles. It is interesting to note that freshly blown hollow Pyrex bulbs gave zero solid-water-air contact angles; these bulbs appeared unstrained when examined in polarized light.

To substantiate the results with stressed specimens, the drop-on-plate method was employed. Compression of a Pyrex glass plate caused the solid-water-air contact angle to increase from zero to about 10° . Release of the compressive force gave a surface which showed a zero contact angle with water. When brass plates were subjected either to compressive or to extensive stress, the solid-water-air contact angle could be increased from a value of 45° to a value of about 60° .

Carefully annealed glass surfaces, giving zero solid-water-air contact angles, when allowed to stand in air showed an increase of contact angle with time of standing (6). Such changes were generally of the order of 15° to 20° for glass, but even greater effects were obtained with advancing angles on metals. Sorption of gases or vapors (5) from the air may have been responsible for these changes.

EFFECT OF HEAT TREATMENT ON SILICA

The effect of heat treatment on solids seemed, from the preliminary tests, to be readily duplicable in the absence of strain. The major portion of the remainder of this investigation has been concerned, therefore, with such effects under diverse, though exactly defined, conditions.

A summary of results obtained with silica against α -bromonaphthalene and against acetylene tetrabromide is given in table 1.

The results illustrate clearly that the previous treatment of the solid is an important factor in determining the size of the contact angle. A fresh silica surface, that is, one that had been prepared by carefully drawing out a large, clear, fused silica rod, showed a moderate hysteresis effect, or difference between the advancing and receding contact angles with α -bromonaphthalene and acetylene tetrabromide. Silica that had been cleaned with hot chromic acid, washed with water, steamed, and dried at 100°C . showed approximately the same effects.

A silica rod that had been heated to 400°C . gave an advancing angle of practically the same value as the receding angle. This change was not permanent, however, for if the silica that had been heated at 400°C . was

allowed to stand for a few hours in dry air the contact angle returned to a value as great as or greater than the original value for the freshly drawn rod. Contact angles could be readily duplicated to $\pm 4^\circ$. The general results obtained were in good agreement with those presented by Bartell and Wooley (1) for similar systems, but obtained by a different method of measurement.

TABLE 1

Advancing and receding contact angles for the systems α -bromonaphthalene-silica-air and acetylene tetrabromide-silica-air

PRETREATMENT	HEAT TREAT- MENT TEMPER- ATURE	TIME OF HEATING	α -BROMONAPHTHA- LENE		ACETYLENE TETRABROMIDE	
			θ_a^*	θ_r^\dagger	θ_a	θ_r
	$^\circ\text{C}$	hours				
Newly drawn surface			12°	5°	19°	14°
Steamed	100	1	13°	6°	21°	16°
Steamed	400	1	6°	5°	15°	14°
Steamed	400	3	0°	0°	15°	14°
Steamed	400	3 $\frac{1}{2}$	15°	6°	22°	15°

* θ_a = advancing contact angle.

$\dagger \theta_r$ = receding contact angle.

\ddagger Then stood in dry air at 25°C . for 12 hours.

EFFECT OF HEAT TREATMENT ON METALS

Gold and platinum were chosen for the study of contact angles on metals. Because of their resistance to corrosion it was believed that surfaces of greater constancy in properties could be obtained with these metals than with less noble metals. When these metals had been heated, both the advancing and receding solid-water-air contact angles were found to have decreased. In order to evaluate if possible the effect of heating upon the behavior of the metal surface, a method of pretreatment of the surface was sought by means of which one might obtain a surface in an easily reproducible condition. The criterion of constancy of surface condition was the solid-water-air contact angle formed on the metal surface.

The surfaces of the metal rods were carefully polished with the edge of a finely ground glass plate, washed briefly in acid, washed thoroughly with water, steamed, and then heated in an oven at 100°C . for one hour. It was found that the surfaces so prepared exhibited with water, within comparatively narrow limits, $\pm 4^\circ$, the advancing and receding angles of contact shown in table 2.

Heating to higher temperatures caused a decrease in both the advancing and receding angles. A fairly wide variation of values was found with some of the systems, which indicated that it was not easy to reproduce, exactly,

surface conditions of the solid. The free surface energies of the solids appeared to change rapidly when exposed to air at room temperature, as was noted by taking contact angle readings at intervals of even a few minutes (6). Metal surfaces differed from silica surfaces in that there was no apparent tendency for receding angles to increase upon exposure of the surface to air for a period of time. It was evident that in a study of metal surfaces great care must be taken to follow given methods of pretreatment so as to prepare standard surfaces for use as surfaces of reference.

TABLE 2
Contact angles of the water-gold and water-platinum systems

TREATMENT	CONTACT ANGLES	
	Gold	Platinum
1. Metal polished, steamed, heated at 100°C. for 1 hour		
Water advancing	70°	63°
Water receding	40°	28°
2. Metal polished, steamed, heated at 600°C. in air for 1 hour		
Water advancing	13°	0°
Water receding	0°	0°
3. Metal polished, steamed, heated at 600°C. in hydrogen for 1 hour		
Water advancing	20°-30°	35°-41°
Water receding	0°	0°
4. Metal polished, steamed, heated at 600°C. in air for 2 hours		
Water advancing	0°	0°
Water receding	0°	0°
5. Metal polished, steamed, heated at 600°C. in air for 2 hours, then 24 hours in air at 25°C.		
Water advancing	65°	
Water receding	0°	0°
6. Metal polished, steamed, heated at 600°C. in air for 1 hour, then 24 hours in air at 25°C		
Water advancing	55°	51°
Water receding	0°	0°

Measurements of interfacial contact angles formed on metals by the interface water-organic liquid were also made. The values obtained varied within fairly wide limits, depending upon the precise pretreatment of the solid, just as did the values for the solid-water-air angles. Data obtained will not be presented in this paper, inasmuch as results have since been obtained for similar systems, but with metal rods that were pretreated in a manner which has been found to give more exact and reproducible results. These results will be presented in an early paper.

SUMMARY

1. A method has been developed for the measurement of contact and interfacial contact angles against either transparent or opaque solids which can be formed into rods. This method is called the vertical-rod method. The method appears to be accurate and can be used to follow adhesion tension changes, and hence gives information concerning free surface energy changes which occur on the surface of solids. The solids studied in this investigation were Pyrex, silica, gold, and platinum.

2. It has been shown that the precise method of pretreatment of a solid surface is important in a study of its surface properties.

3. The presence of strains in glass appears to account for the large water-air contact angles observed on strained glass surfaces. Removal of the strain by careful annealing decreases the contact angle of water on such surfaces to zero.

4. Aging of glass and metal surfaces increases the magnitude of the solid-liquid-air contact angle formed upon them.

5. Heat treatment of solids can greatly alter the magnitude of the contact angle.

REFERENCES

- (1) BARTELL AND WOOLEY: *J. Am. Chem. Soc.* **55**, 3518 (1933).
- (2) BOSANQUET AND HARTLEY: *Phil. Mag.* **42**, 456 (1921).
- (3) COGHILL AND ANDERSON: *J. Phys. Chem.* **22**, 237 (1918).
- (4) LAMPERT: *Kolloid-Z.* **60**, 3 (1932).
- (5) MCBAIN: *Sorption of Gases and Vapours by Solids*. Geo. Routledge and Sons, Ltd., London (1932).
- (6) POCKELS: *Physik. Z.* **15**, 39 (1914).
- (7) SCHULTZ: *Kolloid-Z.* **62**, 294 (1933).
- (8) TOOL AND VALASEK: *Bur. Standards Sci. Papers*, No. 358, p. 537 (1920).

ALTERATION OF THE FREE SURFACE ENERGY OF SOLIDS. II

EFFECT OF HEAT TREATMENT OF METALS IN AIR

F. E. BARTELL AND MIKE A. MILLER

Department of Chemistry, University of Michigan, Ann Arbor, Michigan

Received May 23, 1936

It was shown in a previous paper (2) that the vertical-rod method can be used for the measurement of solid-liquid-air and solid-liquid-liquid contact angles and that it is particularly suitable for obtaining information concerning changes in free surface energy of metals and of other solids which can be obtained in the form of rods. In the present investigation the effect of heat treatment in air on gold, platinum, and steel was studied by means of the vertical-rod method. The liquids used were water, benzene, α -bromonaphthalene, and acetylene tetrabromide, purified according to methods presented in earlier papers from this laboratory.

PREPARATION OF A STANDARD SURFACE

In order to measure the change in the angle of contact formed by a liquid on a metal after heat treatment of the metal, it was necessary that the initial surface condition of the metal be definite and reproducible. A method of pretreatment of gold and platinum was found which gave a standard surface whose solid-water-air contact angle could be reproduced to within $\pm 4^\circ$. The gold or platinum rod was first carefully and completely scraped with the edge of a carborundum crystal, was next polished with the edge of a roughly ground glass plate, and was then polished with a finely ground glass plate until the surface, as observed under a microscope, was practically free of microscopic striations. The rod was handled at all times with clean tin foil. After polishing, it was washed briefly in concentrated hydrochloric acid, then thoroughly with distilled water. It was then steamed for one hour and finally heated at 100°C . in an electric oven in air for one hour. The standard surface gold-water-air contact angle was $68^\circ \pm 4^\circ$. The standard surface platinum-water-air contact angle was $63^\circ \pm 4^\circ$. Only rods giving values within these limits were used for subsequent heat treatment.

Steel, owing to its greater susceptibility to oxidation, did not give a "standard" surface after the same pretreatment as that given to gold and platinum. Various attempts to obtain a standard steel surface were

made, but no satisfactory method of treating steel in air was found. Measurements on heat-treated steel were made, but since no satisfactory reference value was found, data on steel will not be given in this paper.

The thorough polishing given the metals in the pretreatment tends to make the surface entirely amorphous (4). This polishing removes the effects of previous heat treatments so far as the surface is concerned, for, though evidence obtained from the literature (5, 6), as well as from our own experiments, indicates that heat treatment may produce certain specific

TABLE 1

Equilibrium advancing contact angles and adhesion tension values for water on heat-treated gold and platinum

HEAT TREATED FOR 1 HOUR AT	ADVANCING CONTACT ANGLES AND ADHESION TENSION VALUES					
	Gold			Platinum		
	θ_{13}	$\cos \theta_{13}$	A_{13}	θ_{13}	$\cos \theta_{13}$	A_{13}
°C.						
100	68°	0.3746	26.97	63°	0.4540	32.69
200	57°	0.5446	39.21	49°	0.6561	47.24
300	45°	0.7071	50.91	36°	0.8090	58.25
400	36°	0.8090	58.25	25°	0.9063	65.25
500	25°	0.9063	65.25	13°	0.9744	70.16
600	13°	0.9744	70.16	0°		

TABLE 2

Alteration with time of standing in air of equilibrium advancing contact angles and adhesion tension values for water on heat-treated gold

HOURS IN AIR	GOLD PREVIOUSLY HEAT- TREATED AT 100°C. FOR 1 HOUR			GOLD PREVIOUSLY HEAT- TREATED AT 400°C. FOR 1 HOUR			GOLD PREVIOUSLY HEAT- TREATED AT 600°C. FOR 1 HOUR		
	θ_{13}	$\cos \theta_{13}$	A_{13}	θ_{13}	$\cos \theta_{13}$	A_{13}	θ_{13}	$\cos \theta_{13}$	A_{13}
$\frac{1}{2}$	68°	0.375	26.97	36°	0.809	58.25	13°	0.974	70.06
1	69°	0.358	25.81	39°	0.777	55.95	22°	0.927	66.76
5	70°	0.342	24.62	48°	0.669	48.18	38°	0.788	56.74
10	68°	0.375	26.97	50°	0.643	46.28	47°	0.682	49.10
24	71°	0.326	23.44	51°	0.629	45.31	53°	0.602	43.33
120	70°	0.342	24.62	57°	0.545	39.21	55°	0.574	41.30

internal effects as well as surface effects, the surface appears to be affected by internal conditions only if the rod is not sufficiently polished or if it is allowed to stand too long a time before being used after polishing.

CONTACT ANGLE MEASUREMENTS ON HEAT-TREATED GOLD AND PLATINUM IN AIR

The metal rods were first treated so as to obtain the standard surface. They were then heated for one hour at a definite temperature, the tem-

peratures for the different rods ranging in 100°C. steps from 100° to 600°C. $\pm 5^\circ$. The contact angle was measured not later than fifteen minutes after the rod had cooled to room temperature, this length of time being necessary to set up the rod system and to obtain proper focusing of microscope and camera. Measurements were carried out at a temperature of 25°C. $\pm 2^\circ$. The contact angle was photographed and its image was measured directly on the plate or was projected on a screen and measured (2). Table 1 gives the water-air advancing contact angles obtained with heat-treated gold and platinum, and the adhesion tension values, A_{13} , calculated from the cosines of these angles. It will be noted that the angle of contact decreases with progressively higher temperature of heat treatment.

TABLE 3

Interfacial contact angles, metal-water-organic liquid, for heat-treated gold and platinum

HEATED AT °C. FOR 1 HOUR	BENZENE			α -BROMONAPHTHALENE			ACETYLENE TETRABROMIDE		
	θ_{n3}	$\cos \theta_{n3}$	A_{1n}	θ_{n3}	$\cos \theta_{n3}$	A_{1n}	θ_{n3}	$\cos \theta_{n3}$	A_{1n}
Gold									
300	141°	-0.7771	77.88	146°	-0.8290	85.40	138°	-0.7431	79.37
400	113°	-0.3907	71.81	111°	-0.3584	73.16	115°	-0.4226	74.44
500	89°	+0.0175	64.65	86°	+0.0698	62.35	88°	+0.0349	62.88
600	78°	+0.2079	62.95	74°	+0.2756	58.69	83°	+0.1219	65.49
Platinum									
300	123°	-0.5446	77.15	123°	-0.5446	80.91	128°	-0.6157	81.83
400	85°	+0.0872	62.22	83°	+0.1219	60.28	86°	+0.0698	62.58
500	72°	+0.3090	59.44	77°	+0.2250	60.80	75°	+0.2588	60.25
600	61°	+0.4848	(55.18)*	63°	+0.4540	(53.11)*	65°	+0.4226	(55.81)*

* All the A_{1n} values except those marked ()* were calculated from the equation $A_{13} - A_{1n} = S_{n3} \cos \theta_{n3}$ (see reference 3) using the data from tables 1 and 3. The three A_{1n} values marked ()* were calculated from the empirical equation $A_{1n} = (12.8 - S_{n3}) \cos \theta_{n3} + 65.2$ (see reference 1).

When the heat-treated metals stood in air, the contact angle assumed a larger value (2, 7). The rate and magnitude of this change for gold are shown in table 2. Similar data were obtained with platinum. It will be noted that the initial change was very rapid. Such age-change phenomena were probably due to sorption.

WATER-ORGANIC LIQUID INTERFACIAL CONTACT ANGLE MEASUREMENTS ON GOLD AND PLATINUM

Gold and platinum rods were treated to obtain the standard surface, and the interfacial contact angle, metal-water-organic liquid, was measured.

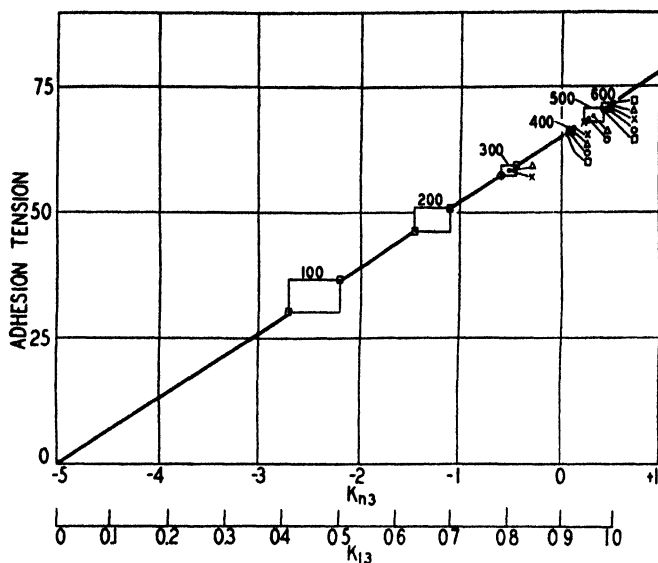


FIG. 1. Change in adhesion tension with heat treatment. Platinum one-quarter of an hour in air. \square , platinum-water-air; Δ , platinum-benzene-water; \circ , platinum-acetylene tetrabromide-water; \times , platinum- α -bromonaphthalene-water.

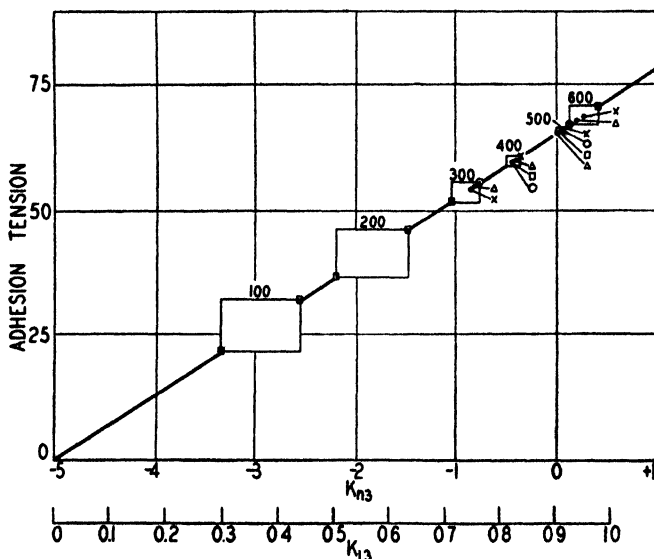


FIG. 2. Change in adhesion tension with heat treatment. Gold one-quarter of an hour in air. \square , gold-water-air; Δ , gold-benzene-water; \circ , gold-acetylene tetrabromide-water; \times , gold- α -bromonaphthalene-water.

The results are presented in table 3. All angles were measured through the water phase. As in the case of the metal-water-air angles, the metal-water-organic liquid angles decreased with increasingly higher temperature of heat treatment. For the three systems of liquids investigated, the interfacial contact angles were approximately the same against a given solid surface, the deviation in most cases being well within the limits prescribed for the standard surface (i.e., $\pm 4^\circ$ for the metal-water-air contact angle).

Since the interfacial angles formed on these metals by the three organic liquids were all practically the same, the empirical equations developed by Bartell and Bartell (1), relating the cosine of the interfacial angle ($\cos \theta_{n3}$)¹

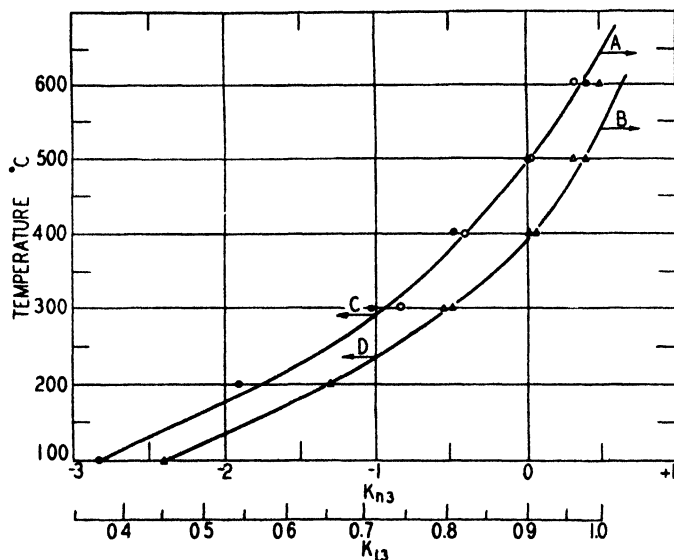


FIG. 3. Change of cosine of contact angle K_{n3} and K_{13} with heat treatment. ●, gold-water-air; ▲, platinum-water-air; ○, organic liquid-water-gold; △, organic liquid-water-platinum.

to adhesion tension, may apply to these metals. That they do apply can readily be shown.

If adhesion tension values, calculated from the observed advancing water-air contact angles on metals after various heat treatments, are plotted against K_{13} , and if the corresponding K_{n3} values for the given heat-

¹ The symbols used in this paper are the same as those used in recent papers from this laboratory, i.e., S represents surface tension, interfacial tension, or free surface energy, A represents adhesion tension, θ the contact angle, and K is the same as the cosine of θ within the limits of $+1$ and -1 , but may take on values greater than $+1$ and less than -1 . The subscripts 1, n , and 3 refer to the solid, any organic liquid, and water, respectively.

treated metals are plotted as a second abscissa scale, the graphs shown in figures 1 and 2 are obtained. The straight line drawn through these points is the so-called "water-line" (1) whose equation is:

$$A_{13} = 12.8K_{n3} + 65.2$$

The area enclosed in the rectangles represents the limits of experimental error for the given temperatures of pretreatment.

If temperature of heat treatment is plotted against K_{13} and against K_{n3} , smooth curves, as shown in figure 3, are obtained. From inspection of these curves it can be seen that gold and platinum, heat-treated at the temperatures corresponding to the ordinates of points *A* and *B*, respectively, should exhibit zero advancing water-air contact angles. Gold and platinum, heat-treated at temperatures corresponding to the ordinates of points *C* and *D*, respectively, should exhibit water-organic liquid interfacial contact angles equal to 180°. This was found experimentally to be correct.

SUMMARY

Rods of gold and platinum were given a special pretreatment so as to have standard surfaces for reference. Such a standard surface could not be produced on rods of steel treated in air. Standard surface rods of gold and platinum were subjected to heat treatment in air at given temperatures ranging between 100° and 600°C., and changes, due to heat treatment, in contact and interfacial contact angles were measured by the vertical-rod method.

With low-temperature treatment the metals were fairly strongly organophilic, while with higher temperature treatments they were less strongly organophilic and could even be caused to become hydrophilic in nature. The changes were probably due to oxidation and recrystallization. The surface properties were found to alter with time of standing after heat treatment.

REFERENCES

- (1) BARTELL AND BARTELL: *J. Am. Chem. Soc.* **56**, 2205 (1934).
- (2) BARTELL, CULBERTSON, AND MILLER: *J. Phys. Chem.* **40**, 881 (1936).
- (3) BARTELL AND OSTERHOF: *Colloid Symposium Monograph* **5**, 113 (1927).
- (4) BEILBY: *Electrochem. Metall.* **3**, 806 (1904).
- (5) CARTER: *Trans. Am. Electrochem. Soc.* **43**, 397 (1923).
- (6) HERSTAD: *Kolloid-Z.* **55**, 169 (1931).
- (7) POCKELS: *Physik. Z.* **15**, 39 (1914).

ALTERATION OF THE FREE SURFACE ENERGY OF SOLIDS. III

EFFECT OF HEAT TREATMENT OF METALS IN A VACUUM AND IN SEVERAL GASES

F. E. BARTELL AND MIKE A. MILLER

Department of Chemistry, University of Michigan, Ann Arbor, Michigan

Received June 6, 1936

Recent communications from this laboratory (2, 3) have shown that large changes in surface properties of metals, caused by heat treatment of the metals in air, can be measured by measurement of the metal-water-air and metal-water-organic liquid contact angles. A method of pretreatment of metals to obtain a standard reference surface has been described (3). This method included polishing and mild heat treatment, both operations being carried out in air.

The present investigation had as its major aim the evaluation of the specific effects of the gas phase during heat treatment of metals. For this investigation a somewhat different method of preparation of standard metal surface was used, since metals polished in air undergo wear oxidation (5, 8) as well as grain or crystal fragmentation (6). Even noble metals such as gold are known to undergo wear oxidation (5) and to be capable of existing in several distinct oxidation patterns (7). For the present investigation standard metal surfaces were prepared by thorough polishing of the metals in an atmosphere of nitrogen and subsequent mild heat treatment in a vacuum. Differences of surface due to different degrees of crystal fragmentation were eliminated by the thorough polishing (4); and the use of a nitrogen atmosphere during polishing and of a vacuum (evacuated from a nitrogen atmosphere) during heat treatment, removed almost entirely the possibility of wear oxidation or heat oxidation.

The experiments on heat treatment of standardized metal surfaces fell naturally into two groups: (a) heat treatment of metals in a vacuum and (b) heat treatment of metals in different gases. In the experiments in a vacuum, gold, platinum, copper, and 18-8 stainless steel were used. In the experiments in gases, silver, aluminum, tungsten, and brass were used in addition to the metals listed above. The gases used were nitrogen, hydrogen, and oxygen. The nitrogen was purified by passing tank nitrogen successively through copper-ammonium carbonate solution, molten phosphorus, a reduced-copper furnace, and suitable drying towers. Oxygen

and hydrogen were carefully dried before being used. The liquids used for contact angle measurements were water, benzene, α -bromonaphthalene, and acetylene tetrabromide, all carefully purified.

PRODUCTION OF STANDARD METAL SURFACES AND MANIPULATION OF THE
VACUUM APPARATUS FOR SOLID-LIQUID-GAS CONTACT ANGLE
MEASUREMENTS

For production of a standard metal surface, the metal rod was drastically polished in air, being handled with clean tin foil at all times. First, it was thoroughly scraped with the edge of a carborundum crystal, then it was polished with the flattened finely ground end of a quartz rod. The metal

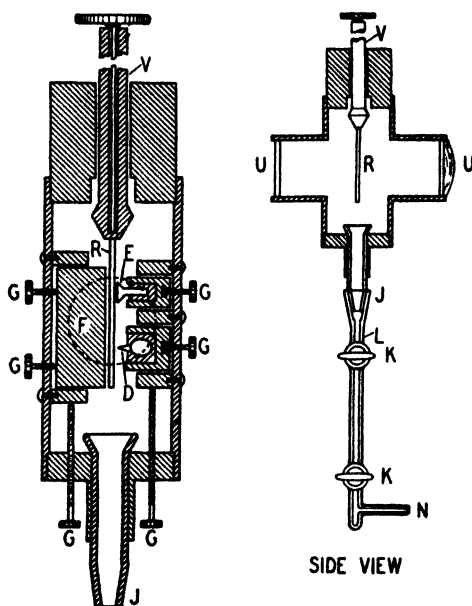


FIG. 1. Polishing apparatus

rod was then placed in the holder, V, figure 1, of the polishing apparatus and nitrogen was allowed to flow through this apparatus for at least one hour. After this the rod was polished in a nitrogen atmosphere in the same way as it had been polished in air, by means of the carborundum crystal, D, and the quartz rod, E. When a surface had been obtained which was practically free of microscopic striations, as shown by examination through the magnifying window, U, of the apparatus, the rod was released from its holder into the lower glass compartment, L, shown in figure 1, side view. In this compartment it was transferred in an atmosphere of nitrogen to the main vacuum apparatus, figure 2.

The vacuum apparatus had previously been swept out with pure nitrogen

for at least one hour by means of a nitrogen line connected at B. With the gas flowing through the apparatus, the heating unit (carrying W, the heating coil) was placed in position. The apparatus was flushed out with nitrogen for another hour after the rod and heating unit were in place. The gas line was then disconnected; stopcock (mercury-seal type) S was closed, and a mercury-seal cap placed over the lower opening, B. The entire unit was then evacuated to a pressure of 10^{-5} mm. of mercury. The electric current was turned on in the heating coil, and the flow of electricity was regulated to a predetermined value. The amount of electricity required

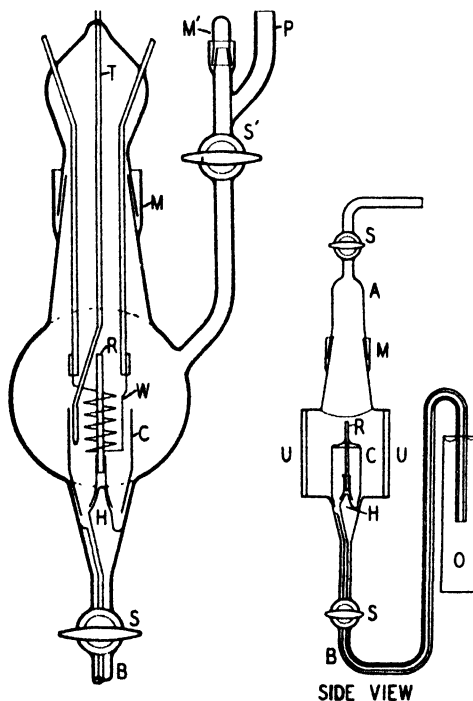


FIG. 2. Main vacuum apparatus

depended upon the temperature of the heat treatment and upon the radiation loss of the apparatus at that temperature. It had to be predetermined for each temperature of heat treatment. The temperature of the metal rods was measured with a calibrated iron-constantan thermocouple, T, in conjunction with a potentiometer and galvanometer. For the pretreatment to give a standard reference surface, this temperature was 100°C .

The time-temperature curve for the approach from 25°C . to the desired temperature of treatment was plotted so that the exact amount of heat energy communicated to the metal could be duplicated in subsequent measurements. When the temperature had attained the constant value of

100°C. (or whatever temperature was being used), the system was allowed to remain thus for exactly one hour, after which the current was turned off and the entire apparatus allowed to cool, the vacuum being carefully replaced with pure nitrogen. The time rate of cooling from a given temperature was made the same for each rod.

A blank run was made before each measurement at the temperature to be used in the measurement proper. This run was made in the hope of eliminating gases dissolved in the glass of the apparatus, which might be given off at the higher temperatures. In this way, it would seem that any gases given off from the glass up to and at the given temperature would be eliminated and pure nitrogen resorbed in their place. In the subsequent measurement at the same temperature, less, or practically no, foreign gases should be evolved from the glass. Nitrogen was kept flowing through the cooled apparatus until it was ready for the measurement proper.

A liquid-air trap was used between the apparatus and the vacuum pump. The vacuum pump was a mercury-vapor pump backed by a high-vacuum oil pump, used in conjunction with a McLeod gauge. All joints and stop-cocks were of the mercury-seal type.

After a rod had been polished and heat treated at 100°C. to bring its surface to the standard reference condition, its surface condition was determined by measurement of the metal-water-nitrogen contact angle. This measurement was carried out in the following manner:

When the rod had cooled to 25°C., the heating unit was removed, with nitrogen flowing through the apparatus, and the unit A (figure 2, side view) attached in its place. The nitrogen line was disconnected, and the siphon attached in its place by means of the ground-glass joint. Water was then siphoned into the glass cup or cell, C, in the apparatus. The advancing contact angle was thus formed. Several measurements could be made on the same rod by raising the siphon reservoir and causing the liquid to advance slightly before each measurement. Lowering the siphon reservoir gave the receding angle. Each angle was either photographed or projected directly onto a special screen for measurement, as described in a previous communication (2). These angles could be readily duplicated to $\pm 2^\circ$. A minimum of three check runs was made on each system investigated. The tabulated results represent the averages of all runs for a given system.

MANIPULATION OF VACUUM APPARATUS FOR THE MEASUREMENT OF SOLID-LIQUID-LIQUID CONTACT ANGLES

For the measurement of solid-liquid-liquid interfacial contact angles, various devices, depending upon the relative glass-wetting characteristics and densities of the two liquids, had to be used in conjunction with the apparatus shown in figure 2. The diagrammatic sketches of such mechan-

ical devices have appeared in a previous paper (2). Except for the use of these additional devices the manipulation of the apparatus was the same as for the measurement of solid-liquid-gas contact angles.

TABLE 1

Alteration of magnitude of contact angles of several metals upon heat treatment of the metals in vacuum

HEATED 1 HOUR IN A VACUUM AT °C	METAL-H ₂ O-N ₂			METAL H ₂ O C ₆ H ₆			METAL-H ₂ O-AcBr ₄			METAL-H ₂ O- α -BrN		
	θ_{12}	K_{12}	A_{12}	θ_{n3}	K_{n3}	A_{1n}	θ_{n3}	K_{n3}	A_{1n}	θ_{n3}	K_{n3}	A_{1n}
Gold												
100	72°	0 309	22 3	180°		(139 3)	180°		(149 0)	180°		(163.5)
200	35°	0 819	59 0	120°	-0 500	76 3	120°	-0 500	78 1	120°	-0 500	79 8
Platinum												
100	65°	0 423	30 4	180°		(125 1)	180°		(133 5)	180°		(145 5)
200	32°	0 848	61 1	108°	-0 309	71 8	109°	-0 326	73 5	109°	-0 326	74 6
Copper												
100	60°	0 500	36.0	180°		(115 5)	180°		(122 8)	180°		(132 0)
150	40°	0 766	55 2	139°	-0 755	81 3	140°	-0 766	84 5	140°	-0 766	88 8
200	28°	0 883	63 6	96°	-0 105	67 2	96°	-0 105	67 6	96°	-0 105	67.9
250	20°	0 940	67 7	80°	0 191	61 0	80°	0 191	60 4	80°	0 191	59.7
18-8 stainless steel												
100	41°	0 755	54 3	144°	-0 809	82 4	146°	-0 829	86 1	144°	-0 809	88 0
150	10°	0 990	70 9	64°	0 438	55 7	64°	0 438	54 1	64°	0 438	52.7
200	0°		(75 3)	40°	0 766	48 6	38°	0 788	45 1	38°	0 788	42 6
250	0°		(76 2)	32°	0 848	46 8	30°	0 866	43 7	31°	0 857	40 9

* The symbols used in this paper are the same as those used in recent papers from this laboratory, i.e., S represents surface tension, interfacial tension, or free surface energy, A represents adhesion tension, θ the contact angle, and K is the same as the cosine of θ within the limits of +1 and -1, but may take on values greater than +1 and less than -1. The subscripts 1, n , and 3 refer to the solid, any organic liquid, and water, respectively. AcBr₄ = acetylene tetrabromide; α -BrN = α -bromonaphthalene. Values in parentheses were extrapolated from diagram.

ALTERATION OF MAGNITUDE OF CONTACT ANGLES OF METALS ON HEAT TREATMENT OF THE METALS IN A VACUUM

The results of the investigation of contact angle changes on heat treatment of metals in a vacuum are given in table 1. All the angles given in

table 1 are "equilibrium" advancing angles. The metal-water-nitrogen angle for a given metal heat-treated in a vacuum decreased in a regular manner with increasing temperature of heat treatment. For a given temperature of heat treatment the magnitude of this angle for the different metals varied in the order of their apparent reactivity. This might seem to indicate oxide film formation, due to the presence of traces of oxygen during the heating process, since progressive oxide film formation would give increasingly hydrophilic surfaces and decreasing contact angles with water. No temper colors, i.e., no visible indications of an oxide film, were noted, however, on any of the metals, even when they were treated for

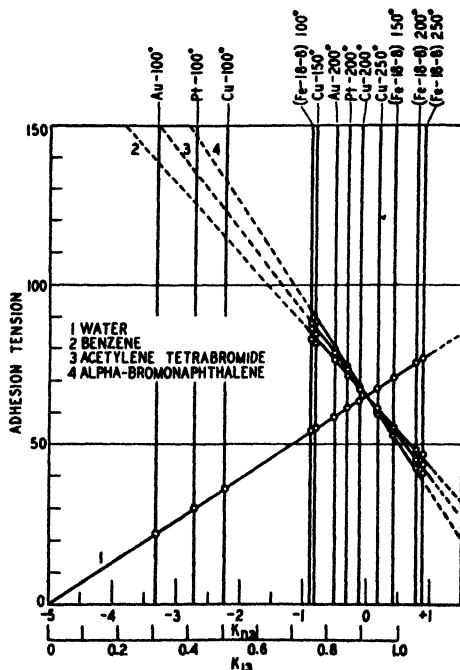


FIG. 3. K_{n3} versus adhesion tension

long periods of time at over 400°C. in the vacuum apparatus. It seems more probable, therefore, that heat oxidation had been eliminated in the vacuum apparatus, and that the decrease in the contact angle was caused by changes in the crystal structure of the metal during the heat treatment. Sorption of nitrogen by the metals probably also took place.

For the three different liquid-liquid systems tested, the interfacial contact angles on a given metal, heat-treated at a given temperature in a vacuum, were all the same within the limits of experimental error. The empirical equations of Bartell and Bartell (1) may then apply to these metals heat-treated in a vacuum. When the data obtained are plotted on

a K_{ns} versus adhesion tension graph, as shown in figure 3, the points lie in straight lines whose equations are the equations cited above.

The progressive alteration of the contact angles of metals heat-treated in a vacuum is in accordance with results previously obtained for heat treatment of metals in air (3), and lends assurance to the previous conclusion that crystallization phenomena are in part responsible for such changes.

METHOD OF HEAT TREATMENT OF METALS IN DIFFERENT GASES

Standard surface rods were polished in the given gas in the apparatus shown in figure 1, transferred in an atmosphere of that gas to an especially designed induction furnace, and heated for one hour at 200°C. in the same gas at atmospheric pressure. The furnace was so designed that the rod could be loaded into it from the transferring unit, L, of the polishing apparatus, without coming into contact with air. The rod was freely suspended in the interior of the furnace without more than 2 mm. contact with any solid, i.e., the glass of the furnace interior. The current of gas entered from the rear to facilitate loading without introduction of foreign gases. After heating, the rods were removed by a special holder into a cooling compartment through which the given gas was flowing, and after rapid cooling to 25°C., transferred to the main apparatus, figure 2, which had previously been flushed out with the same gas. The measurements of contact angles were made in an atmosphere of this gas at atmospheric pressure. With surfaces treated in this manner, the contact angle could be checked in the majority of cases to $\pm 4^\circ$.

ALTERATION OF MAGNITUDE OF CONTACT ANGLES OF METALS HEAT-TREATED IN DIFFERENT GASES

Some of the results obtained with metals heated in nitrogen and in hydrogen are given in table 2. For these metal-water-nitrogen and metal-water-hydrogen systems the angles formed showed no tendency to change over relatively long periods of time and were, apparently, equilibrium angles.

Table 3 gives the initial metal-organic liquid-nitrogen and the metal-organic liquid-hydrogen advancing contact angles for metals heated in nitrogen and in hydrogen, respectively. These initial angles are contact angles obtained immediately after immersion of the cooled metal rod into the organic liquid. They are finite, reproducible, advancing contact angles, but they decrease to zero angles with time. Somewhat analogous effects were obtained with rods which had been heated in oxygen.

Heating the metal rods in hydrogen or nitrogen apparently caused such a profound change in the surface structure (and, hence, in the free surface energy) that chemical reaction took place between the metal and the halogenated organic liquids used in this investigation. When such

TABLE 2

Contact angles of water on several metals and alloys heat-treated in various gases at 200°C. for one hour

METAL	METALS HEATED IN NITROGEN			METALS HEATED IN HYDROGEN		
	Metal-water-nitrogen angles			Metal-water-hydrogen angles		
	θ_{12}	K_{12}	A_{12}	θ_{12}	K_{12}	A_{12}
Gold	80°	0.174	12.5	56°	0.559	40.3
Platinum	58°	0.530	38.2	42°	0.743	53.3
Silver	69°	0.358	25.8	48°	0.669	48.2
Copper	90°	0.000	0.0	66°	0.407	29.3
Steel (18-8)	78°	0.208	15.0	60°	0.500	36.0
Aluminum	74°	0.276	19.8	70°	0.342	24.6
Tungsten	40°	0.766	55.2	68°	0.375	27.0
Brass	110°	-0.342	-24.6	43°	0.731	52.7

TABLE 3

Initial contact angles of organic liquids on several metals and alloys heat-treated in various gases at 200°C. for one hour

METAL	HEATED IN NITROGEN ATMOSPHERE						HEATED IN HYDROGEN ATMOSPHERE		
	Metal-acetylene tetrabromide-nitrogen			Metal- α -bromonaphthalene-nitrogen			Metal-acetylene tetrabromide-hydrogen		
	θ_{1n}	K_{1n}	A_{1n}	θ_{1n}	K_{1n}	A_{1n}	θ_{1n}	K_{1n}	A_{1n}
Gold	30°	0.866	42.4	8°	0.990	44.6	0°		
Platinum	0°			0°			0°		
Silver	12°	0.978	47.9	0°			0°		
Copper	34°	0.829	40.6	12°	0.978	43.0	0°		
Steel (18-8)	26°	0.899	44.0	0°			0°		
Aluminum	22°	0.927	45.4	0°			25°	0.906	44.5
Tungsten	0°			0°			20°	0.940	46.2
Brass	45°	0.707	34.6	16°	0.961	42.3	0°		

TABLE 4

Comparison of contact angles of water on gold and on platinum heat-treated one hour at 200°C. in a vacuum and in several gases

HEATED IN	GOLD			PLATINUM		
	θ_{12}	K_{12}	A_{12}	θ_{12}	K_{12}	A_{12}
Vacuum	35°	0.819	59.0	32°	0.848	61.1
Hydrogen	56°	0.559	40.3	42°	0.743	53.3
Air	57°	0.5446	39.21	49°	0.6561	47.24
Nitrogen	80°	0.174	12.5	58°	0.559	38.2

heat-treated rods were immersed in α -bromonaphthalene or in acetylene tetrabromide which had previously been saturated with water, metallic bromides were formed with those metals which exhibited finite initial contact angles. Metallic bromides were not formed with metals whose initial contact angle was zero.

Though one is not justified in calculating adhesion tension for a system which is not in equilibrium, adhesion tension values calculated from the initial advancing metal-organic liquid contact angles given in table 3 are some linear function of the adhesion tension of the corresponding metal-water-air contact angles (table 2). It is impossible, at present, to assign a precise meaning to such relations.

In table 4 the effects of heating gold and platinum in a vacuum and in several gases are compared through comparison of the metal-water-gas contact angles and the corresponding adhesion tensions. Gold and platinum are made progressively less hydrophilic by heat treatment in a vacuum, in hydrogen, in air, and in nitrogen, in the order given. For those solids to which the Bartell-Bartell (1) equations apply, a decrease in hydrophilic properties indicates a corresponding increase in organophilic properties. That these heat-treated metals have been made progressively organophilic is indicated by the fact that the least hydrophilic of them, the gold heated in nitrogen, actually reacted with α -bromonaphthalene and with acetylene tetrabromide.

SUMMARY

1. Rods of gold, platinum, copper, 18-8 stainless steel, silver, aluminum, tungsten, and brass were pretreated so as to have standard reference surfaces.

2. Heat treatment of the metals in a vacuum caused them to become more hydrophilic with increasing temperature of heat treatment.

3. The metals became progressively less hydrophilic when heat treated in a vacuum, in hydrogen, in air, and in nitrogen, in the order stated.

4. All the metals except platinum and tungsten, when heat treated in nitrogen, readily reacted chemically with acetylene tetrabromide; gold, copper, and brass, similarly heat treated, reacted with α -bromonaphthalene. Aluminum and tungsten, heat treated in hydrogen, reacted with acetylene tetrabromide.

5. The wetting characteristics of the different metals differ greatly, and the wetting characteristics of surfaces of the same metal differ greatly, depending upon the precise pretreatment of the metal.

REFERENCES

- (1) BARTELL AND BARTELL: J. Am. Chem. Soc. **56**, 2205 (1934).
- (2) BARTELL, CULBERTSON, AND MILLER: J. Phys. Chem. **40**, 881 (1936).

- (3) BARTELL AND MILLER: J. Phys. Chem. **40**, 899 (1936).
- (4) BEILBY: Aggregation and Flow of Solids. Macmillan and Co., Ltd., London (1921).
- (5) FINK: Trans. Am. Soc. Steel Treating **18**, 204 (1930).
- (6) GOSS: Trans. Am. Soc. Steel Treating **17**, 241 (1930).
- (7) OUELLET AND RIDEAL: J. Chem. Physics **3**, 150-8 (1935).
- (8) ROSENBERG AND JORDON: Bur. Standards J. Research **13**, 267 (1934), Research Paper No. 708.

THE SOLUBILITY RELATIONSHIPS IN MIXTURES OF BRASSIDIC ACID WITH ERUCIC ACID, METHYL BRASSIDATE, AND ETHYL BRASSIDATE¹

L. J. P. KEFFLER AND A. M. MAIDEN

Department of Chemistry, University of Liverpool, Liverpool, England

Received March 26, 1936

INTRODUCTION

Some years ago, Timmermans and Viseur (19) made a thorough study of various binary mixtures of geometrical isomers and found that, in conformity with Bruni's rule, the *trans*-compounds showed a decidedly greater tendency than the *cis*-compounds to form mixed crystals with the corresponding saturated compounds. They therefore, along with Bruni, attributed to the saturated compounds a configuration similar to that of the *trans*-forms.

Shortly thereafter, Skau and Saxton (17) investigated mixtures of the two β -chlorocrotonic acids and found that the ideal solution law applied very closely.

No work of precision has, however, been done on mixtures of *cis-trans* isomers of high molecular weight, such as erucic and brassidic acids and their esters. Mascarelli and Sanna (12), it is true, have found that erucic and brassidic acids form a simple eutectic system, but, owing to the lack of purity of their preparations, their results need to be confirmed before they can be used for testing the applicability of the ideal solution law.

There is another problem upon which an accurate study of such mixtures may throw light, as will appear from the following considerations: Smith (18) finds that ethyl palmitate and ethyl stearate form mixed crystals, as do also hexadecane and octadecane, while hexadecyl iodide and octadecyl iodide form a system containing a compound with a non-congruent melting point. According to Bhatt, Watson, and Patel (2), such compounds are formed also in the following systems: caproic-stearic, lauric-myristic, lauric-stearic, stearic-behenic, and palmitic-stearic acids and in the system methyl palmitate-methyl stearate; but the pairs lauric acid-lignoceric acid, methyl laurate-methyl myristate, and methyl stearate-methyl behenate give simple eutectic diagrams.

¹ This article is part of a thesis submitted by A. M. Maiden to the Faculty of Science of the University of Liverpool in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

On the other hand, Müller and Shearer (14) have proved by means of x-rays that the saturated fatty acids crystallize in double molecules, while Francis, Piper, and Malkin (4) have shown that compound formation occurs in equimolecular mixtures of such acids differing from each other by one, two, or three carbon atoms, the mixtures melting like a pure compound. Malkin (10) has established further that the methyl esters of the saturated fatty acids crystallize in double molecules, but are also characterized by a metastable form which crystallizes in single molecules. The ethyl esters were found to crystallize always in single molecules.

Thus it would appear that mixtures of substances of high molecular weight, which do not differ too much in carbon content and which crystallize in double molecules, yield phase-rule diagrams showing the presence of a compound with a non-congruent melting point. The exceptions to this rule, as exemplified by the systems methyl stearate–methyl behenate and methyl laurate–methyl myristate, may be apparent rather than real, for the results of Bhatt and coworkers (2) were obtained by cooling methods, which are liable in many cases to give erroneous data, as will be indicated in the course of the discussion of the results reported in this paper.

Since Müller and Shearer have shown that both erucic and brassidic acid crystallize also in double molecules, it is of interest to see whether a careful examination of their mixture will, from the point of view of the phase rule, show the presence of a molecular compound. The difference in their configuration would indeed not be expected to interfere with the considerations given above, as compound formation between these molecules appears to be a matter of the terminal groups only of the carbon chain.

An investigation of the systems of the type acid–ester might also prove interesting in view of the difference found by Malkin (10) in the states of aggregation of the acids and methyl esters as against that of the corresponding ethyl esters. Two such systems will be examined in the present paper.

APPARATUS

Figure 1 shows a cross section of the apparatus, which recalls in many respects that of Andrews, Kohmann, and Johnstone (1) and that of Skau and Saxton (17), except that it was so designed that the specimens might be kept *in vacuo* during each experiment, in view of their unsaturation and consequent liability to rapid oxidation.

The specimens (weighing 1.5 g.) were contained in small test tubes (internal diameter 1 cm.) connected with an exhausting tube by means of a short length of stout rubber tubing; this was surrounded by a split brass sleeve, tightened by a "Jubilee" circular clip. The melt was stirred by means of a miniature glass ring stirrer, attached by means of a stout platinum wire to a soft iron armature working inside a solenoid spool made of brass.

Temperatures were measured to within $0.1^{\circ}\text{C}.$ by means of a two-junction, copper-eureka thermoelement, calibrated at every 10° from $20^{\circ}\text{C}.$ to $90^{\circ}\text{C}.$ against a standard thermometer. The E.M.F. was measured on a Cambridge thermoelectric potentiometer used in conjunction with a 400-ohm Cambridge "Ayrton-Mather" galvanometer. Fractions of $100\text{ }\mu\text{ volts}$ were obtained by the deflection method, whilst during all readings the potentiometer was frequently balanced against a standard cell. This electrical measuring system, which allowed readings to be taken to within $5\text{ }\mu\text{ volts}$ (corresponding to $0.05^{\circ}\text{C}.$), was entirely and adequately shielded against leaks from high potential circuits by supporting it throughout on metal, all the metal supports being electrically connected.

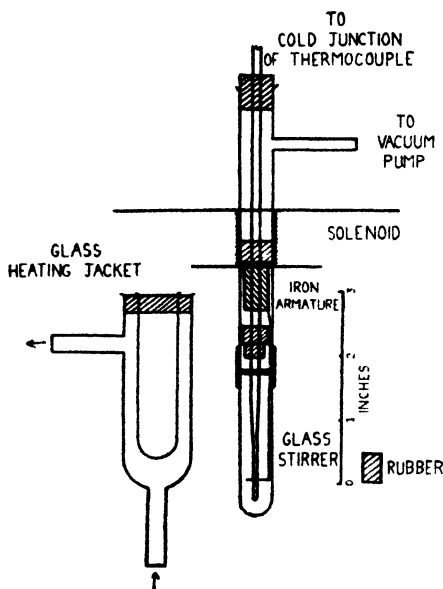


FIG. 1. The apparatus

For the determination of cooling curves the specimen was surrounded by a double-walled metal jacket, through which water at any convenient temperature was circulated from a thermostat.

For the determination of the melting point, the metal jacket was replaced by a double-walled glass jacket (see figure 1). In this manner the specimen was observed through only a thin layer of water and yet, as the thermostat contained 30 liters of water, very fine control over the rate of heating could be obtained.

TECHNIQUE

Mixtures of definite composition were made up by direct weighing into the specimen tubes, the total weight of the mixture being always 1.5 g.

The contents of the tubes were then just melted and well mixed, the tube placed on the apparatus, and the specimen allowed to set *in vacuo*. The mixture was now remelted and once more allowed to set *in vacuo*, so as to avoid completely the dissolution of gases as impurities.²

The type of system being dealt with was determined by taking cooling curves of the various mixtures prepared, the E.M.F. of the thermoelement being noted at regular time intervals. It was found that the convergence temperature for this apparatus was considerably below the temperature of the jacket, so that the method of correction of Andrews, Kohmann, and Johnstone (1) for the supercooling was inapplicable. As the mixtures showed in many cases considerable supercooling, this method could not in any case have been used with any satisfaction; the freezing points of the systems were therefore determined by observing the temperature at which the last crystal in the melt disappeared (cf. Johnstone and Jones (7), Smith (18), and Skau (16)). This temperature could be easily determined by means of the glass heating apparatus described. The specimen was heated rapidly until only a small portion remained solid, the glass jacket was then raised so as to surround the melt, and water at a temperature slightly below the expected melting point was circulated from the thermostat. The temperature of this water was now slowly raised, and when the details of the thermoelement wires could be seen clearly, the E.M.F. of the element was noted as the melting point. It was found that the last crystals disintegrating under the action of the stirrer gave a cloudy suspension. Very efficient agitation of the melt during such a determination is obviously necessary.

The results thus obtained are considered to be within 0.1°C . of the true freezing point. Repeat determinations always agreed to 0.05°C .

Eutectic temperatures were fixed by taking heating curves of mixtures which possessed very nearly the eutectic composition (as seen from the melting point-composition diagram). The procedure followed was similar to that for cooling curves, water slightly above the expected eutectic temperature being circulated through the brass jacket.

CONTROL OF PURITY FOR THE SUBSTANCES USED

The preparation and purification of the substances required for this research have already been described elsewhere (9).

The melting points and setting points of these substances were found

² Such gases cause the molten specimen to froth if it is allowed to set under reduced pressure after exposure to the atmosphere. The fact that such substances, when in the molten state, are capable of dissolving appreciable quantities of gas from the atmosphere does not seem to have received very much notice in the past, although it must play an important rôle in the rate of oxidation of the substance (see, however, reference 6).

to be within $0.1^{\circ}\text{C}.$, except in the case of ethyl brassidate, where the difference was $0.2^{\circ}\text{C}.$, probably as a result of the complication due to extensive creeping. This coincidence of melting points and setting points is probably the most sensitive criterion of purity for long-chain compounds, particularly for the saturated ones, where there is no other available.³

In the case of unsaturated substances, the control of the purification should always be supplemented by the precise determination of the iodine values (8).

The results of such control of purity for the substances examined are shown in table 1.

RESULTS

System erucic acid-brassicidic acid (see table 2 and figure 2)

Erucic and brassidic acids were found to have only one form in the region investigated. Mixtures containing up to 81 per cent erucic acid gave the

TABLE 1
Purity of the substances examined

SUBSTANCE	IODINE VALUE		SETTING POINT	MELTING POINT
	Observed	Theoretical		
			$^{\circ}\text{C}$	$^{\circ}\text{C}.$
Brassicidic acid	74.7	75.0	59.8	59.75
Erucic acid	74.0	75.0	33.25	33.35
Methyl brassidate	71.2	72.1	30.0	30.1
Ethyl brassidate	68.7	69.3	24.8	25.0

normal cooling curve of a simple eutectic system, while for mixtures richer in erucic acid, the cooling curves were of a different type. Coincident with

³ The determination of the setting point alone does not always provide a sufficiently unambiguous guarantee of purity. For instance, after purifying a specimen of brassidic acid by removal of several per cent of impurities, the setting point increased only by $0.1^{\circ}\text{C}.$, but the iodine number went up from 74.2 to 74.7. In another case further purification was accompanied by a rise of iodine number from 73.6 to 74.2 for the same small increase in setting point of $0.1^{\circ}\text{C}.$ However, the melting point appears to be, at least in some cases, more sensitive than the setting point to the presence of impurities; e.g., while two specimens of methyl brassidate had the same iodine number and the same setting point, one of them melted as high as $32.35^{\circ}\text{C}.$, against $30.1^{\circ}\text{C}.$ for the other specimen.

The melting point may thus be used with advantage as a further control of purification, either with or without the simultaneous determination of the setting point. This will especially be the case when the compound examined is very nearly pure, and when the eutectic in the system compound-impurity lies very near 100 per cent pure compound.

this change, the phenomenon of a double melting point appeared. For example, by allowing a mixture containing 83.5 per cent of erucic acid to cool for some time after freezing had set in, one observed a melting point of 39.1°C., whilst if the melting point was taken immediately after freezing occurred, 30.7°C. was obtained. (Both results were repeatable.)

An increase of the erucic acid content to 87.0 per cent caused the cooling curve to become double-humped if determined with the specimen unseeded; for a specimen which was not completely melted, a cooling curve similar to that corresponding to 83.5 per cent of erucic acid was obtained.

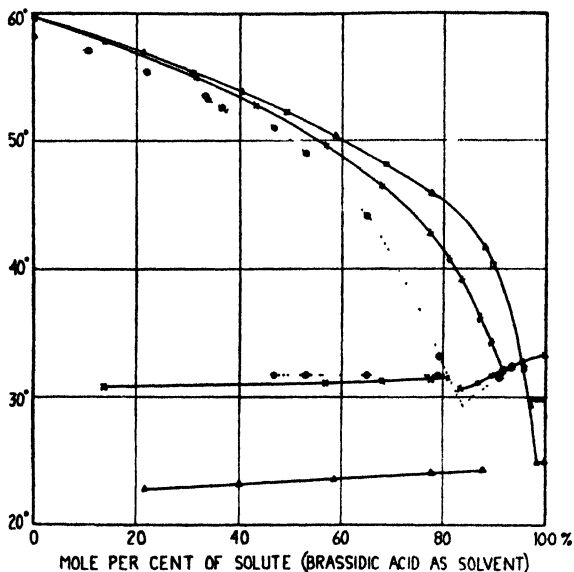


FIG. 2. Cooling curves. X, the system brassidic acid-erucic acid (O for the results of Mascarelli and Sanna); □, the system brassidic acid-methyl brassidate; △, the system brassidic acid-ethyl brassidate.

In this case, the specimen had a melting point of 31.2°C. if cooled until a few crystals appeared and then remelted; but if cooled until completely solid and then remelted, it was necessary to heat to 36.2°C. before the last crystal disappeared. Thus the change which occurred spontaneously with the 83.5 per cent mixture required nuclei to be present for it to occur with the 87.0 per cent specimen. As the higher melting point undoubtedly lies on the brassidic acid solubility curve, it would seem that the second hump corresponds to the crystallization of brassidic acid and the first to the crystallization of erucic acid.

Supercooling increases as the percentage of erucic acid in the mixture increases, and with 83.5 per cent of erucic acid the crystallization of the latter evidently occurs before that of the brassidic acid. In this case,

therefore, the metastable erucic acid solubility curve can be followed up over a large range.

It is this particular phenomenon which renders it imperative to determine the melting points of these mixtures rather than their freezing points by the normal method, if the correct phase-rule diagram is to be constructed. It also caused Mascarelli and Sanna (12) to think that the eutectic mixture was about 80 per cent erucic acid, these workers not cooling to completion any mixture showing this phenomenon.

The eutectic temperature determined from the heating curves of the specimens containing 92 per cent and 89.6 per cent of erucic acid was 31.8–31.9°C., whilst the composition of the eutectic mixture determined from the melting point-composition diagram was 90.5 per cent erucic acid.

TABLE 2
The system brassidic acid-erucic acid

COMPOSITION IN MOLE PER CENT OF ERUCIC ACID	$\log_{10} N$	SOLID PHASE	MELTING POINT		$10^6/T$
			°C	°K.	
0	0	Brassidic acid	59 80	332 8	3005
13.8	−0 064	Brassidic acid	57 85	330 8	3023
31.5	−0 164	Brassidic acid	55 10	328 1	3048
42.8	−0 243	Brassidic acid	52 80	325 8	3069
57.0	−0 366	Brassidic acid	49 65	322 7	3099
67.8	−0 492	Brassidic acid	46 45	319 5	3130
77.5	−0 648	Brassidic acid	42 75	315 8	3167
81.0	−0 721	Brassidic acid	40 70	313 7	3187
83.5	−0 782	Brassidic acid	39 10	312 1	3204
83.5	−0.078	Erucic acid	30 70	303 7	3294
87.0	−0 886	Brassidic acid	36 15	309 2	3234
87.0	−0 060	Erucic acid	31 15	304 2	3287
89.6	−0.983	Brassidic acid	34 20	307.2	3255
89.6	−0 048	Erucic acid	31.60	304.6	3283
91.2	−0.040	Erucic acid	31 95	305.0	3279
92.0	−0.036	Erucic acid	32 10	305.1	3278
95.1	−0 022	Erucic acid	32 60	305 7	3272
100	0	Erucic acid	33 25	306.3	3265

Mixtures containing more than 90.5 per cent of erucic acid have a melting point independent of the history of the specimen, as here it is normal for the erucic acid to crystallize out first.

The cooling curves of these mixtures show primary crystallization of erucic acid, but no eutectic halt, the crystallization of brassidic acid being unduly delayed. The heating curves, however, are those normally shown by mixtures with compositions near that of the eutectic.

The melting point-composition diagram, as determined for the present work, contrasts with that obtained by Mascarelli and Sanna (12) as shown

in figure 2 (dotted curve). The displacement (towards the left) of the right-hand side of their diagram, caused by supercooling, is very evident.

The system ethyl brassidate-brassidic acid (see table 3 and figure 2)

The cooling curves of mixtures of brassidic acid with 22.0, 50.4, 59.1, 77.9, and 88.4 per cent of ethyl brassidate are those of a simple eutectic system. Those of mixtures containing 96.3 per cent and 98.4 per cent of ethyl brassidate are similar to that of the mixture of the previous system containing 83.5 per cent of erucic acid, but have no slight halt corresponding to a low melting point.

This type of curve is due to great supercooling, which causes the mixtures to behave as though they were richer in solute than they actually are, mixtures weaker than the eutectic mixture behaving like a eutectic mixture and setting at one temperature.

TABLE 3
The system brassidic acid-ethyl brassidate

COMPOSITION IN MOLE PER CENT OF ESTER	$\log_{10} N$	SOLID PHASE	MELTING POINT		$10^4/T$
			$^{\circ}\text{C.}$	$^{\circ}\text{K.}$	
0	0	Brassidic acid	59.80	332.8	3005
22.0	-0.108	Brassidic acid	57.00	330.0	3030
40.4	-0.225	Brassidic acid	54.15	327.2	3056
59.1	-0.389	Brassidic acid	50.65	323.7	3089
77.9	-0.657	Brassidic acid	46.00	319.0	3135
88.4	-0.934	Brassidic acid	41.80	314.8	3177
96.3	-1.434	Brassidic acid	32.50	305.5	3274
97.4	-1.589	Brassidic acid	29.45	302.5	3306
98.4	-1.803	Brassidic acid	24.90	297.9	3357
100		Ethyl brassidate	25.05		

All these mixtures have a single melting point.

The melting point-composition diagram for the mixture of ethyl brassidate and brassidic acid is notable for its asymmetry, this being sufficient to render the exact determination of the eutectic a difficult matter. The mixture containing 98.4 per cent of ethyl brassidate was assumed to have the eutectic composition.

Ethyl brassidate creeps to a remarkable extent when setting, and only starts to freeze after considerable supercooling. The cooling curve of the pure material always rises very slightly instead of remaining level during setting. For this reason the melting point instead of the setting point was used in the construction of the melting point-composition diagram.

No evidence of a second crystalline form of the ester was found.

Near the eutectic point, the brassidic acid solubility curve is so steep

that the separation in a solid state of a very small amount of brassidic acid greatly influences the melting point of the mixture, it thus being very difficult to determine the exact melting points in this region. It is also clear that a cooling curve investigation in this region must be absolutely useless.

The system methyl brassidate-brassidic acid (see table 4 and figure 2)

The cooling curves of mixtures of brassidic acid with 30.9, 49.3, 68.9, and 89.4 per cent of methyl brassidate are those of a simple eutectic system; those of mixtures containing 96.2 and 97.5 per cent of methyl brassidate are similar to those of mixtures containing 96.3 and 98.4 per cent of ethyl brassidate.

Again the exact position of the eutectic point is difficult to ascertain. The melting point-composition diagram indicates that it is between 97.5

TABLE 4
The system brassidic acid-methyl brassidate

COMPOSITION IN MOLE PER CENT OF ESTER	$\log_{10} N$	SOLID PHASE	MELTING POINT		$10^4/T$
			°C.	°K.	
0	0	Brassidic acid	59.80	332.8	3005
30.9	-0.161	Brassidic acid	55.65	328.7	3042
49.3	-0.295	Brassidic acid	52.65	325.7	3070
68.9	-0.508	Brassidic acid	48.50	321.5	3110
89.4	-0.975	Brassidic acid	40.40	313.4	3191
96.2	-1.420	Brassidic acid	32.60	305.6	3273
97.5	-1.606	Brassidic acid	30.10	303.1	3299
98.4		Ester	30.05		
100		Ester	30.10		

and 98.4 per cent methyl brassidate, a heating curve of the 89.4 per cent mixture gives 29.85°C. as the temperature, while the two solubility curves cut at 29.8°C. and 97.7 per cent.

Pure methyl brassidate supercools considerably before setting, but it does not creep. Its cooling curve remains level during setting, and does not rise as in the case of ethyl brassidate.

No second form of methyl brassidate was found.

DISCUSSION

(A) The brassidic acid solubility curves in the systems methyl brassidate-brassidic acid and ethyl brassidate-brassidic acid are so remarkably similar that the two melting point-composition diagrams can be superimposed for the whole of the range (from 0 to 97 per cent) of concentrations (figure 2). One is thus led to the conclusion that methyl and ethyl

brassicates have, when dissolved in brassidic acid, the same state of aggregation (cf. Malkin (10)).

This solubility curve of brassidic acid with respect to either ester lies only very slightly above that for the system brassidic acid-erucic acid, which tends to indicate that erucic acid, when in solution in brassidic acid, is in a state of aggregation identical with or at least very similar to that of the alkyl brassidates.

In none of the diagrams investigated is there any trace of compound formation. This, from the evidence given in the introduction, supports the assumption that all these substances exist in solution in the simplest possible molecules.

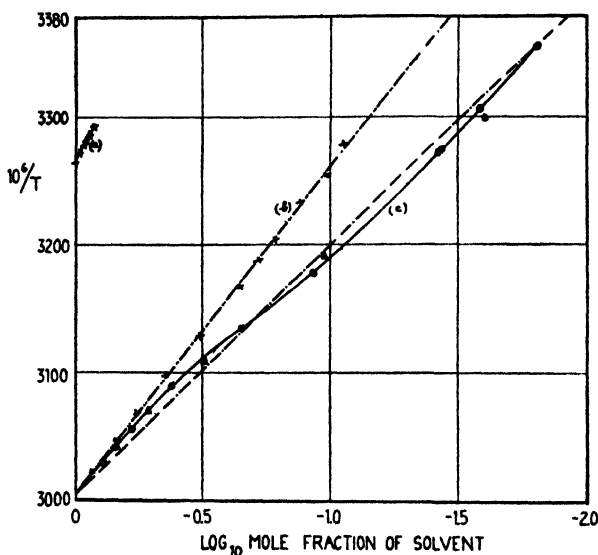


FIG. 3. Solubility curves. Curve a, brassidic acid in erucic acid; curve b, erucic acid in brassidic acid; curve c: \odot , ethyl brassidate in brassidic acid; Δ , methyl brassidate in brassidic acid.

(B) It has been stated by various authors (see, e.g., Johnstone (7)) that, provided the constituents of binary mixtures of certain types of isomers are not too much alike, the plot of $\log N$ (where N is the mole fraction of the solute) against $1/T$ (where T is the absolute freezing point of the mixture) is a straight line. If, however, the constituents are very similar, mixed crystals are formed.

In order to form an opinion as to whether the pairs of substances investigated here form, or do not form, ideal solutions, the results have been plotted in the form $\log_{10} N$ against $10^6/T$ (figure 3).

For the system brassidic acid-erucic acid points from the erucic acid solubility curve lie on a straight line (figure 3, curve a), while the points

from the brassidic acid solubility curve (figure 3, curve b) lie on a straight line up to 83.5 per cent erucic acid, after which the solubility of brassidic acid increases more rapidly than the ideal solution law would indicate.

The fact, however, that a straight line is obtained for such a large proportion of the diagram when the results are computed in the manner described indicates that erucic and brassidic acids have the same molecular complexity in solution in each other and behave to a large extent as ideal solutes; in particular it is evident that there is no change in their state of aggregation with change in concentration.

Only the points for the brassidic acid solubility curve can be obtained from the ester diagrams. These, when plotted, lie on one S-shaped curve (figure 3, curve c). According to Mortimer (13) this type of curve is obtained in systems in which one component is polar and the other is non-polar, and where there is a great difference in the internal pressures. Unfortunately there are no data from which the internal pressures of these esters may be calculated. When the internal pressures of the acids themselves are calculated from the data of Semeria and Ribotti-Limone (15), values in the neighborhood of 400 atmospheres at 90°C. are found for both acids.

These authors determined the parachors of these two acids, and obtained values dependent upon temperature, a fact which would tend to show the presence of some association in these pure liquids. The results here reported show that no such association occurs.

Waentig and Pescheck (20) have inferred from freezing-point measurements that lauric and palmitic acids exist, to some extent, as double molecules when dissolved in carbon tetrachloride.

Our results for the ester systems show the danger of basing conclusions upon freezing-point depressions alone (see, for example, Bruni and Gorni (3)). The freezing-point depressions for the esters dissolved in brassidic acid are smaller than the ideal solution law would indicate. This might have been interpreted as evidence of solid solution formation; the determination of the cooling curves of the system showed, however, that this did not occur.

Thus while the true freezing point cannot be obtained with these systems from cooling-curve determinations, such measurements must be carried out for fixing the type of system being investigated.

The heat of fusion of brassidic acid, calculated from the slope of the $\log_{10} N_{\text{brassidic}}$ versus $10^6/T$ curve for the system brassidic acid-erucic acid is 18.0 kg-cal. per mole, while that of erucic acid, calculated similarly from the $\log_{10} N_{\text{erucic}}$ versus $10^6/T$ curve, is 12.3 kg-cal. per mole. Mascarelli (11), by similar means (using the normal freezing-point method and formula), found 17.8 and 12.1 kg-cal. per mole, respectively. As these methods do not permit of any great accuracy, the divergence between these results is within the experimental error.

These values, when compared with that determined calorimetrically by Garner and King (5) for behenic acid, namely 18.6 kg-cal. per mole, add further support to Bruni's contention that the structures of brassidic and behenic acids must be very similar.

On the other hand, Müller and Shearer have shown (14) that the long spacings of erucic and behenic acids are practically the same, while that of brassidic acid is much greater. From this it might have been expected that the heats of crystallization of erucic and behenic acids would have been closer to each other than those of the latter and of brassidic acid, instead of what has been found from the phase-rule diagrams. This remark shows that there must be, as has often been emphasized for other compounds, a very close relation between the heat of crystallization and the melting point, and that the length of the crystal cell plays only a secondary rôle in determining the magnitude of the heat of crystallization.

SUMMARY

1. An apparatus for the accurate determination of phase-rule diagrams for mixtures of long-chain compounds has been described. It has been found that melting points rather than cooling curves must be determined with these systems.

2. The systems brassidic acid-erucic acid, brassidic acid-methyl brassidate, and brassidic acid-ethyl brassidate have been investigated. All are simple eutectic systems. The brassidic acid solubility curves in the ester systems are superimposable.

3. The ideal solution law holds in the case of brassidic acid and erucic acid, but not for the ester systems; these latter give an S-shaped curve for the $\log_{10} N$ versus $1/T$ plot, the solubility of brassidic acid in this system being always less than the ideal solubility.

4. Evidence has been obtained that all these compounds exist in the simplest possible molecules in the liquid state.

5. No evidence for the existence of a second crystalline form of any of these compounds could be obtained.

6. The solubility of gases from the atmosphere in these compounds has been emphasized.

In conclusion the authors wish to thank Prof. E. C. C. Baly, F.R.S., for facilities granted, and the Imperial Chemical Industries, Ltd., whose United Alkali Scholarship was held by one of them (A. M. M.).

REFERENCES

- (1) ANDREWS, KOHMANN, AND JOHNSTONE: *J. Phys. Chem.* **29**, 915 (1925).
- (2) BHATT, WATSON, AND PATEL: *J. Indian Inst. Sci.* **13A**, 141 (1930).
- (3) BRUNI AND GORNI: *Atti accad. Lincei* [5] **8**, 454.
- (4) FRANCIS, PIPER, AND MALKIN: *Proc. Roy. Soc. London* **133A**, 214 (1930).

- (5) GARNER AND KING: J. Chem. Soc. **1929**, 1849.
- (6) GARNER AND RYDER: J. Chem. Soc. **127**, 727 (1928).
- (7) JOHNSTONE AND JONES: J. Phys. Chem. **32**, 592 (1928).
- (8) KEFFLER AND MAIDEN: J. Soc. Chem. Ind. **52**, 242T (1933).
- (9) KEFFLER AND MAIDEN: Bull. soc. chim. Belg. **44**, 467 (1935).
- (10) MALKIN: J. Chem. Soc. **1931**, 2796.
- (11) MASCARELLI: Gazz. chim. ital. [2] **45**, 209 (1915).
- (12) MASCARELLI AND SANNA: Gazz. chim. ital. [2] **45**, 335 (1915).
- (13) MORTIMER: J. Am. Chem. Soc. **45**, 633 (1923).
- (14) MÜLLER AND SHEARER: J. Chem. Soc. **123**, 2043 (1923).
- (15) SEMERIA AND RIBOTTI-LIMONE: Gazz. chim. ital. **60**, 862 (1930).
- (16) SKAU: J. Am. Chem. Soc. **52**, 945 (1930).
- (17) SKAU AND SAXTON: J. Am. Chem. Soc. **50**, 2693 (1928).
- (18) SMITH: J. Chem. Soc. **1931**, 802; **1932**, 737.
- (19) TIMMERMANS: Bull. soc. chim. Belg. **36**, 179 (1927).
TIMMERMANS AND VISEUR: Bull. soc. chim. Belg. **35**, 426 (1926).
- (20) WAENTIG AND PESCHECK: Z. physik. Chem. **93**, 529 (1919).

ADDITION COMPOUNDS OF PHOSPHOROUS ACID WITH CERTAIN ORGANIC COMPOUNDS¹

H. L. REDFIELD AND G. B. KING

Laboratory of General Chemistry, The State College of Washington, Pullman, Washington

Received June 13, 1936

In a previous communication (5) it has been shown that orthophosphoric acid forms addition compounds with several types of organic compounds; furthermore, Kendall's (2) rule of acidity held in all systems examined. It was the purpose of the present investigation to make a comparison of phosphorous and phosphoric acids with regard to their ability to form addition compounds with organic substances and to test further the validity of Kendall's rule of acidity.

In the study of these addition compounds, two methods have been employed. The most direct method is the determination of freezing-point curves in two-component systems. This method has certain advantages in that the compound is isolated, and furthermore the composition may be determined from the phase diagram. The second method of study is described by Knox and Richards (6). This method is based on the fact that strong acids added to solutions of weak acids decrease the solubility of the latter because of common-ion effect. In certain cases, however, decrease in solubility takes place to a certain point only, after which an increase in solubility occurs. This increase in solubility is attributed to compound formation.

EXPERIMENTAL

Phosphorous acid was obtained from Eimer and Amend and purified by recrystallization. The recrystallized acid melted at 74.4°C. (corrected), which is higher than previously reported. Most of the organic compounds used in this investigation were prepared by the Eastman Kodak Co., and in only a few cases was any special purification necessary.

The method of experimentation in determining freezing points has previously been given (5).

¹ The material of this paper was presented by Herbert L. Redfield in partial fulfillment of the requirements for the degree of Master of Science in Chemistry at The State College of Washington.

The solubilities of several organic acids and phenol were determined in solutions of progressively greater concentrations of phosphorous acid. About 20 cc. of the solution of phosphorous acid was placed in a large test tube, together with an excess of the solute. The tube and contents were heated to 50° to 60°C. for a short time to near saturation. The tube was then placed in a thermostat at 25°C., and the contents stirred several times daily for a period of ten days to two weeks. This was found to be a sufficient length of time for attainment of equilibrium. Portions of the samples were then pipetted off and analyzed.

METHODS OF ANALYSIS

Although several methods of analysis have been employed by other investigators, the method by which the solvent acid is determined gravimetrically and the solute acid by difference from total acidity, proved satisfactory. It was found that phosphorous acid could be oxidized quantitatively with concentrated nitric acid to which a small amount of hydrochloric acid was added, after which the phosphorus was determined as magnesium pyrophosphate. Total acidity was determined by titration with standard sodium hydroxide, using phenolphthalein as indicator. The end point is reasonably sharp.

For analysis of the phenol-phosphorous acid mixture, the phenol was precipitated as tribromophenol and weighed as such. The procedure was as follows: A suitable aliquot containing from 0.08 to 0.2 g. of phenol was diluted to 25 cc. and bromine water added slowly with rapid stirring. The phosphorous acid was oxidized slowly with the excess bromine. Any tribromophenol bromide formed is changed to tribromophenol by the phosphorous acid. The former bromine compound is yellow, while the latter is white. The precipitate was transferred to a Gooch crucible, washed, and dried over phosphorus pentoxide to constant weight. This method gave results which were uniformly 2.6 per cent low; however, by carefully standardizing the procedure and applying the above correction, very satisfactory results were obtained. The phosphorous acid was determined gravimetrically.

The oxalic acid was determined directly by titration with potassium permanganate after calcium oxalate had been precipitated in a buffered acetic acid solution.

EXPERIMENTAL RESULTS

The results of the freezing-point determinations are given in table 1 and of the solubility determinations in table 2.

The compounds used were considered representative for studies of binary systems to test further the rule of acidity. Curves are shown in figure 1. No evidence of compound formation was found in any of the

Freezing-point data

MOLE PER CENT H ₂ PO ₃	FREEZING POINT	MOLE PER CENT H ₂ PO ₃	FREEZING POINT	MOLE PER CENT H ₂ PO ₃	FREEZING POINT
Acetic acid		Pyruvic acid— <i>Cont'd</i>		Acetophenone— <i>Cont'd</i>	
	°C.		°C.		°C.
100	73.2	56.2	45.7	24.7	16.7
92	68.3	51.8	42.8	20.5	17.1
85.9	64.0	51.3	43.2	16.5	17.7
79.8	60.0	48.2	40.6	11.2	18.3
73.7	55.2	43.9	38.1	5.7	19.0
68.5	51.0	39.1	34.4	0.0	19.7
63.7	47.4	33.4	31.3		
58.4	42.7	30.1	29.3	Piperonal	
53.8	38.7	24.8	24 (±0.5)	100	73.0
47.4	33.4	20.4	19. (±1.0)	91.5	68.4
42.8	28.4	12.7	7 (±2.0)	87.2	66.2
36.9	23.2	Phenol		81.4	63.2
31.2	17.7			77.2	60.0
27.4	13.5	100	73.6	73.1	56.6
26.0	13.5	93.0	70.0	69.4	53.2
25.6	13.2	87.8	68.0	64.5	49.2
24.8	11.0	83.5	66.7	58.1	42.2
20.0	10.0	78.1	65.0	54.1	38.6
14.3	11.7	72.8	64.1	53.0	37.3
7.8	13.6	68.4	63.0	51.8	36.2
0.0	16.4	66.8	62.7	46.2	32.8
		63.5	62.0	40.8	32.9
Trichloroacetic acid		59.8	61.1	37.0	30.7
100	73.6	55.6	60.3	34.3	31.1
92.4	69.7	44.6	57.5	29.0	32.0
85.0	67.8	40.7	56.7	23.9	32.6
80.2	66.4	36.9	56.2	18.4	33.2
75.7	65.2	33.4	55.4	13.9	33.8
70.0	64.1	30.4	54.2	8.8	34.2
66.4	63.3	26.9	53.8	0.0	35.1
61.5	61.9	22.4	51.1	Coumarin	
56.3	60.7	17.9	48.9	100	74.5
53.7	60.3	13.5	45.9 (36.2)	90.4	69.4
50.8	59.7	7.9	37.6	82.4	63.6
48.6	58.9	0.0	40.6	77.1	59.0
43.3	57.3	Acetophenone		72.4	53.3
38.3	55.2			68.6	47.5
33.3	53.6	100	73.1	66.6	44.5
26.9	50.9	94.0	70.0	62.3	39.3
22.0	49.0	82.8	63.8	58.8	40.4
18.0	50.0	78.0	60.1	54.8	43.7
14.2	51.0	72.2	55.3	50.8	48.8
8.9	52.7	67.4	51.0	49.8	50.5
0.0	57.2	61.7	45.0	45.9	54.6
		56.9	40.3	41.6	57.8
Pyruvic acid		51.9	35.2	37.7	60.1
100	72.8	47.2	30.2	32.8	62.1
85.3	63.8	42.8	26.3	30.1	63.1
81.0	60.7	41.2	24.9	25.0	64.2
75.8	57.6	37.8	19.3	20.1	65.3
70.2	54.4	34.6	17.5	14.0	66.4
65.6	51.7	31.7	16.1	8.1	67.3
60.4	48.2	28.6	16.3	0.0	68.7

TABLE 2

Solubility data: normalities of solvent and solute when varying concentrations of solvent are saturated with the solute

SAMPLE NO.	OXALIC ACID		CITRIC ACID		SUCCINIC ACID		PHENOL	
	$C_2H_2O_4$	H_3PO_3	$C_6H_5O_7$	H_3PO_3	$C_4H_4O_4$	H_3PO_3	C_6H_5OH	H_3PO_3
	<i>N</i>	<i>N</i>	<i>N</i>	<i>N</i>	<i>N</i>	<i>N</i>	<i>N</i>	<i>N</i>
1	2.407		12.61		1.347		0.896	
2	1.71	8.48	11.42	6.18	0.90	9.79	0.808	9.59
3	1.51	12.78	9.13	11.64	0.69	16.61	0.881	16.02
4	1.38	15.11	8.07	15.21	0.71	18.60	0.918	17.99
5	1.21	18.38	6.15	21.02	0.75	25.55	1.060	22.95
6	1.13	20.21	5.12	25.61	1.34	34.20	1.214	26.65
7	1.00	23.39	3.70	30.77	1.51	35.97		
8	0.77	30.77	2.66	37.38				
9	0.71	36.66	2.22	41.42				
10	0.81	42.02						
11	0.84	44.73						

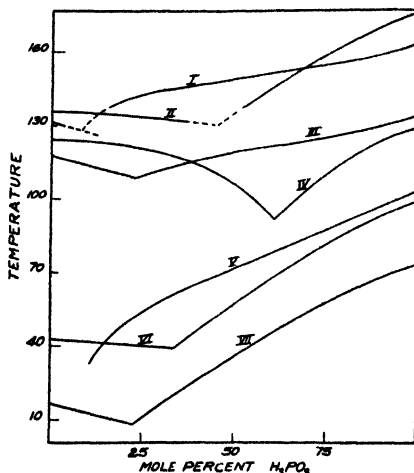


FIG. 1. Freezing points of binary systems of phosphorous acid and certain organic compounds. Curve I, phenol and phosphorous acid; subtract 90 from temperature scale. Curve II, piperonal and phosphorous acid; subtract 100 from temperature scale. Curve III, trichloroacetic acid and phosphorous acid; subtract 60 from temperature scale. Curve IV, coumarin and phosphorous acid; subtract 55 from temperature scale. Curve V, pyruvic acid and phosphorous acid; subtract 30 from temperature scale. Curve VI, acetophenone and phosphorous acid; subtract 25 from temperature scale. Curve VII, acetic acid and phosphorous acid.

above systems. Although some difficulty was encountered in determining freezing points in some of the systems, particularly in the region of the

eutectic, still they are sufficiently accurate to leave little doubt as to the non-existence of a compound.

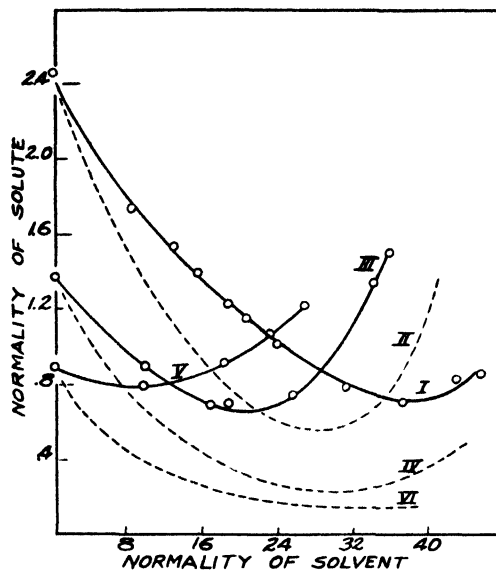


FIG. 2. Solubility curves of binary systems. Curve I, oxalic acid in phosphorous acid. Curve II, oxalic acid in phosphoric acid. Curve III, succinic acid in phosphorous acid. Curve IV, succinic acid in phosphoric acid. Curve V, phenol in phosphorous acid. Curve VI, phenol in phosphoric acid. Curves II, IV, and VI are taken from data of Kepfer and Walton (4).

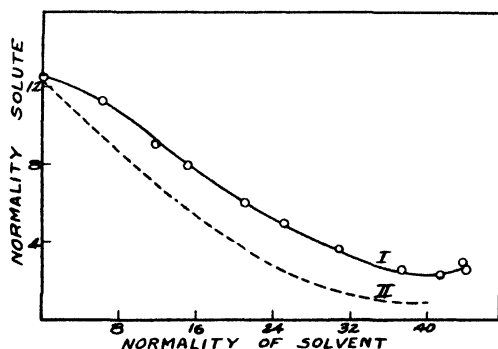


FIG. 3. Solubility curves of binary systems. Curve I, citric acid in phosphorous acid. Curve II, citric acid in phosphoric acid (taken from data of Kepfer and Walton (4)).

Curves for the various systems are shown in figures 2 and 3. For the purpose of comparison, the curves for phosphoric acid taken from data of

Kepfer and Walton (4) are shown. In all cases there appears to be definite evidence of the formation of addition compounds.

DISCUSSION

From the results of this investigation it appears that phosphorous acid forms addition compounds only in solution. Also Kendall's rule of acidity is borne out well in the solubility study, but in this case is not successful in predicting compound formation in freezing-point studies of phosphorous acid with a second component.

On the basis of Kendall's rule, phosphorous acid would be expected to form addition compounds, as it is of the same approximate strength as phosphoric acid, which yielded several compounds in a similar study of freezing-point curves. As a matter of fact, since phosphorous acid is slightly stronger, the tendency for compound formation should be slightly greater with certain organic compounds. However, Kendall's rule at best is a qualitative one and the results obtained here indicate that factors other than acidic strength, such as structure and nature of compounds involved, must play a not inconsiderable rôle in compound formation. Too, it is questionable that acid dissociation constants which have been determined in water solution should be carried over to a solvent other than water. However, Kendall's rule is well borne out in the solubility study, in which curves very similar to the ones formed in a similar solubility study with phosphoric acid are found. For purposes of comparison the curves obtained in the study with phosphoric acid are included in figures 2 and 3. The primary dissociation constants of the acids concerned in this study follow:

<i>Acid</i>	<i>K</i>
Oxalic acid (8).....	3.8×10^{-2}
Citric acid (10).....	8.0×10^{-4}
Succinic acid (9) ..	6.7×10^{-5}
Phenol (3).....	1.08×10^{-10}
Phosphorous acid (7)	$1.6 \text{ to } 6.2 \times 10^{-2}$
Phosphoric acid (1).....	1.1×10^{-2}

Compounds were indicated in every case. Assuming sharpness of break as indicative of relative tendency toward compound formation, phenol and succinic acid show the greatest tendency to form addition compounds with phosphorous acid, while citric and oxalic acids show a lesser tendency. This is to be expected in view of Kendall's rule, since the difference in acidic strengths between phosphorous acid and oxalic and citric acids is less than the difference between phosphorous acid and succinic acid and phenol.

When a comparison of phosphorous and phosphoric acids is made, generally speaking, phosphorous acid shows a slightly greater tendency to

form addition compounds than phosphoric acid. Again this is in agreement with Kendall's rule.

It is to be noted that although phenol exhibits an unusually strong tendency toward compound formation in solution, no evidence whatever is obtained in a freezing-point study. This directly bears out the statement that phosphorous acid appears to form these addition compounds only in solution.

SUMMARY

1. The freezing-point diagrams of several binary systems in which phosphorous acid acts as one component have been determined. No compound formation was indicated.

2. The solubilities of phenol, oxalic acid, succinic acid, and citric acid have been determined in solutions of phosphorous acid of varying concentration.

3. Kendall's rule of acidity holds well in solution, but in the case of phosphorous acid fails in freezing-point equilibria.

4. A comparison of solubility curves of phosphorous and phosphoric acids has been made.

5. The melting point of phosphorous acid was recorded as 74.4°C. (corrected).

REFERENCES

- (1) ABBOTT AND BRAY: *J. Am. Chem. Soc.* **31**, 729 (1909).
- (2) KENDALL, J.: *J. Am. Chem. Soc.* **43**, 1545 (1921).
- (3) KENDALL, J.: *J. Am. Chem. Soc.* **39**, 7 (1917).
- (4) KEFFER AND WALTON: *J. Phys. Chem.* **34**, 543 (1930).
- (5) KING AND WALTON: *J. Phys. Chem.* **35**, 1745 (1931).
- (6) KNOX AND RICHARDS: *J. Chem. Soc.* **115**, 508 (1919).
- (7) KOLTHOFF: *Rec. trav. chim.* **46**, 350 (1927).
- (8) LANDOLT-BÖRNSTEIN: *Physikalisch-chemische Tabellen*, Vol. II, p. 1133. J. Springer, Berlin (1923).
- (9) OSTWALD: *Z. physik. Chem.* **3**, 282 (1889).
- (10) WALKER: *J. Chem. Soc.* **61**, 696 (1892).

A FURTHER STUDY OF THE EFFECT OF SUGAR ALCOHOLS AND THEIR ANHYDRIDES ON THE DISSOCIATION OF BORIC ACID

JOHN C. KRANTZ, JR., C. JELLEFF CARR, AND FRANCES F. BECK

Department of Pharmacology, School of Medicine, University of Maryland, Baltimore, Maryland

Received June 6, 1936

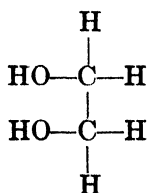
INTRODUCTION

Studies on the influence of mannitol and dulcitol and certain of their anhydrides on the dissociation of boric acid were reported in a previous communication (7). In general, the increased dissociation of boric acid produced by sugar alcohols was exhibited to a lesser degree or not at all by their anhydrides. Another series of these substances has been made available for study, and further investigations as to the effect of these compounds on the dissociation of boric acid have been instituted.

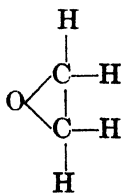
MATERIALS

The inositol, erythritol, pentaerythritol, and adonitol employed were Pfanstiehl's c.p. products and met the specifications of their catalogue. Ethylene glycol, ethylene oxide, propylene glycol, propylene oxide, and trimethylene glycol were supplied by the Eastman Kodak Co. The dihydroxyacetone employed was Oxantin, prepared formerly by Merck and Co. The epihydrin alcohol was prepared from epibromhydrin (1). The *l*-epihydrin alcohol, distilling at 70°C. at 10 mm. pressure, was employed. The polygalitol was extracted from *polygala amara* (9). The compound melted at 138°C. (uncorrected). The erythritan was prepared from erythritol by dehydration with sulfuric acid (2, 6). Analysis gave the following composition: carbon, 45.21 per cent; hydrogen, 7.56 per cent. The calculated values are: carbon, 46.15 per cent; hydrogen, 7.69 per cent.

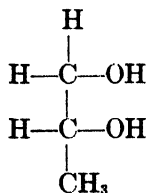
The following formulas indicate the structural relationship existing among these compounds.



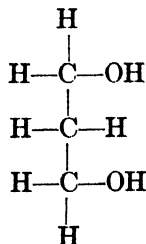
Ethylene glycol



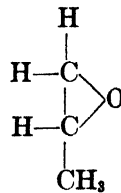
Ethylene oxide



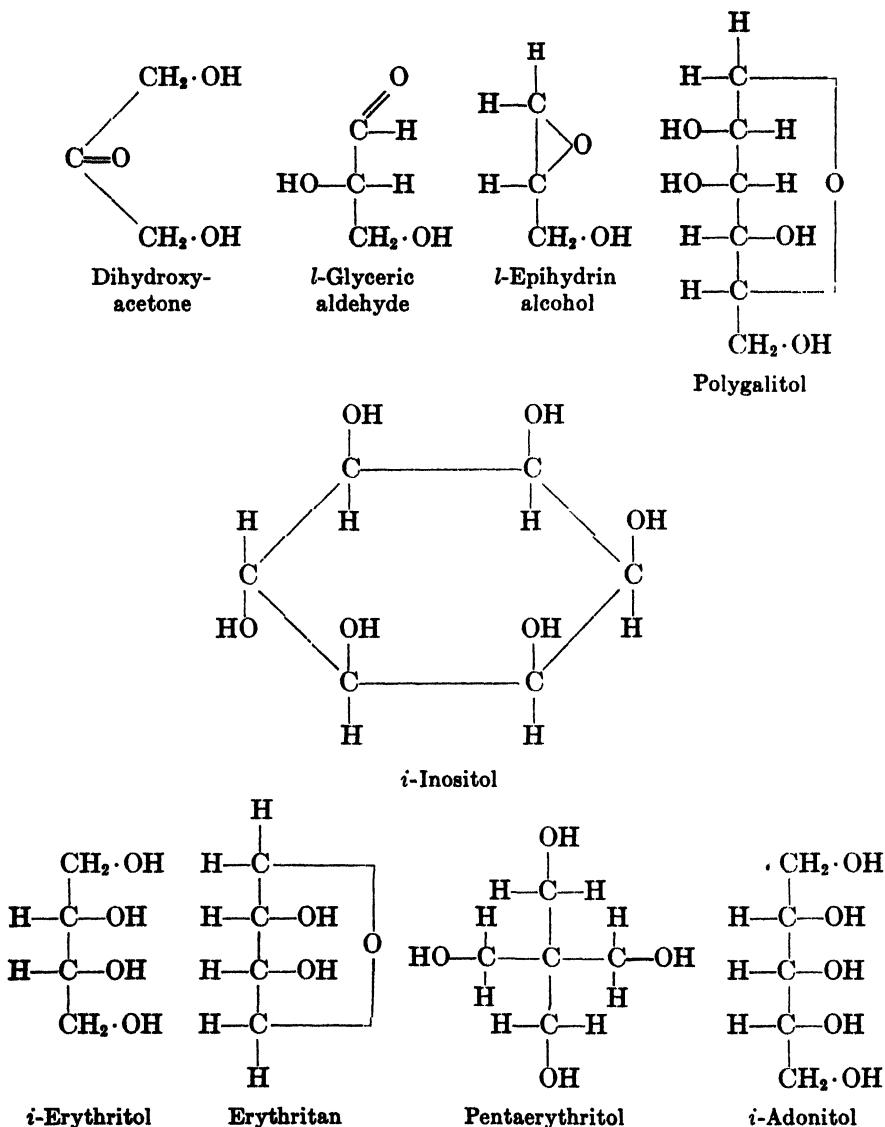
Propylene glycol



Trimethylene glycol



Propylene oxide



METHODS

The solutions of the various compounds studied contained 4 g. of compound in 100 cc. of 0.1 molar boric acid. To 10-cc. portions was added 0.1 normal sodium hydroxide in quantities varying from 1 cc. to 12 cc. Immediately after the addition of the alkali the pH of the solution was determined electrometrically at $25^{\circ} \pm 0.5^{\circ}\text{C}.$, using the Wilson-type electrode (11). The results are set forth in figure 1.

DISCUSSION

An examination of the graph shows that the substances studied divide themselves readily into three classes. Class 1 contains those compounds which do not affect the dissociation of boric acid. In this class, ethylene glycol, ethylene oxide, both propylene glycols, *l*-epihydrin alcohol, and propylene oxide occur. As glycerol affects the dissociation of boric acid, a

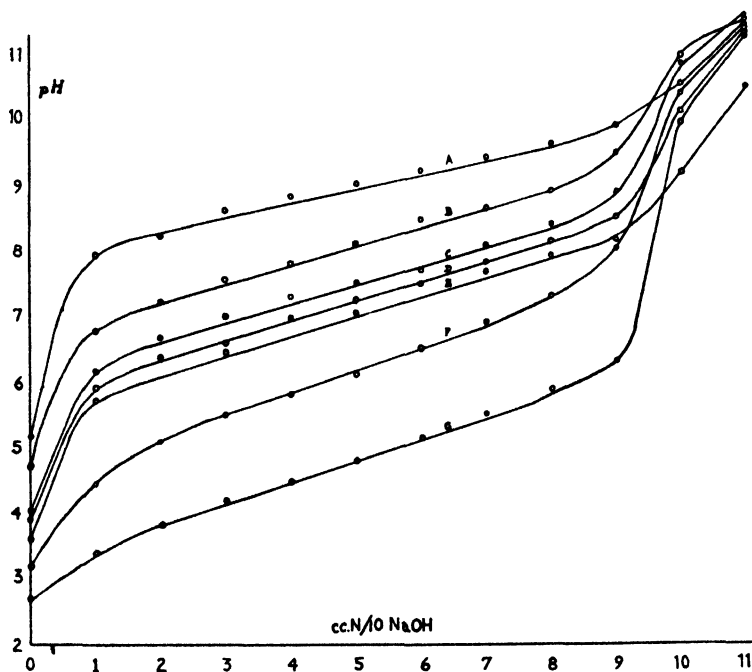


FIG. 1. The effect of sugar alcohols on the dissociation of boric acid. Curve A, $M/10$ boric acid; curve B, $M/10$ boric acid + 4 per cent glycerol; curve C, $M/10$ boric acid + 4 per cent erythritol; curve D, $M/10$ boric acid + 4 per cent adonitol; curve E, $M/10$ boric acid + 4 per cent dihydroxyacetone; curve F, $M/10$ boric acid + 4 per cent mannitol; curve G, $M/10$ boric acid + 4 per cent erythritan.

Class 1 substances corresponding to curve A: ethylene glycol, ethylene oxide, propylene glycol, trimethylene glycol, propylene oxide, *l*-epihydrin alcohol, polygalitol, and *i*-inositol. Class 2 substances corresponding approximately to curves C, D, and E: erythritol, pentaerythritol, adonitol, glyceric aldehyde, and dihydroxyacetone. Class 3: erythritan.

summary of the results on these compounds would indicate that at least three hydroxyl groups on adjacent carbon atoms are necessary for a potentiation of the dissociation of boric acid, as neither propylene glycol nor trimethylene glycol influences it. Polygalitol, the 1,5 anhydride of mannitol, likewise does not affect the dissociation, yet mannitan, which is the 1,4 anhydride of mannitol, produced an intermediate effect be-

tween mannitol and polygalitol. Thus, by extending the oxide ring to include the hydroxyl group on the fourth carbon atom, the effect on boric acid is lost. Inositol, which is essentially cyclic mannitol—namely, with two hydroxyl groups in the ring—likewise falls into class 1.

The second class includes those substances which affect boric acid with approximately the same dissociation potentiation as does mannitol. This class includes erythritol, pentaerythritol, adonitol, glyceric aldehyde, and dihydroxyacetone. The first three compounds require no special comment. By virtue of their respective structures they fall into the general classification of substances studied by Böseken (4) and recommended for study by van Liempt (10), i.e., those compounds having hydroxyl groups on the same side of adjacent carbon atoms. Dihydroxyacetone definitely differs from this class of substances, yet it strikingly potentiates the dissociation of boric acid with an effect equal to that of its isomer, glyceric aldehyde. Of special interest is the fact that the aldose and the ketose possess greater potentiation power than does the sugar alcohol, glycerol. Owing to the fact that crystalline dihydroxyacetone occurs in a dimeric form, the substance was subsequently resolved to its monomeric form by melting (3) and a second titration curve was prepared with the solution of the melted compound. The dimeric and monomeric curves were practically identical. The greater potentiation of the dissociation of boric acid exhibited by the aldose and ketose than that produced by glycerol seems to indicate that an aldehyde or a ketone group present in the molecule augments the potentiation by the hydroxyl groups. Mellon and Norris (8) have shown that the ketohexose fructose is more effective in potentiating the dissociation of boric acid than the isomeric aldohexose, glucose. In the trioses, dihydroxyacetone and glyceric aldehyde, the aldehyde and the ketone groups have equal value.

The third class contains only erythritan. Erythritan, 1,4-anhydroerythritol, with but two hydroxyl groups in the molecule and these enclosed in an oxide ring, is unique among the substances studied in this investigation. In addition it seems to be foremost among the compounds potentiating the dissociation of boric acid recorded in the literature. In a 4 per cent solution, its downward displacement of the titration curve of boric acid is greater than that of its mother substance, erythritol, with two more hydroxyl groups in the molecule, and also greater than that of the isomeric hexahydroxy sugar alcohols, mannitol, dulcitol, and sorbitol. In our previous studies (7) with the anhydrides of mannitol and dulcitol and in this work with 1,5-anhydromannitol, the removal of a molecule of water from the sugar alcohol with the formation of the oxide ring diminished greatly or obliterated its action on the dissociation constant of boric acid. In this regard erythritan is a striking exception. The results of Böseken and his students indicate that in the sugar alcohols the increase in poten-

tiation of the dissociation of boric acid varies with the number of hydroxyl groups in the molecule. Erythritan reverses this concept. This observation was considered so unusual that the compound was prepared by another method, namely, by the dehydration of erythritol by heating in a sealed tube (2). The compound after three distillations exhibited a pH of 6.6 in 1 per cent aqueous solution and affected the dissociation of boric acid to the same degree as did the substance prepared from erythritol by the action of concentrated sulfuric acid. The structure of the anhydride was established by Grimaux and Cloez (5) by demonstrating its relationship to furfuran.

CONCLUSIONS

1. The effect of a number of sugar alcohols, related compounds, and anhydrides of sugar alcohols upon the dissociation of boric acid has been studied.

2. In general, the anhydrides of the sugar alcohols potentiate the dissociation of boric acid to a lesser degree than do the sugar alcohols themselves. Erythritan is dissimilar in this respect, exerting an effect greater than either erythritol or mannitol.

3. Propylene glycol has no effect on the dissociation of boric acid. The introduction of a ketone or aldehyde group into the molecule with the formation of dihydroxyacetone and glyceric aldehyde, respectively, potentiates the dissociation of boric acid to a greater degree than does glycerol with three hydroxyl groups in the molecule.

REFERENCES

- (1) ABDERHALDEN AND EICHWALD: *Ber.* **48**, 1847 (1915).
- (2) BECK, F. F.: *The Fate of Erythritol and Erythritan in the Animal Body*. Thesis, University of Maryland, 1936.
- (3) BERTRAND: *Compt. rend.* **129**, 341 (1899); *Beilstein*, Vol. I, p. 846.
- (4) BÖESEKEN, J.: *Rec. trav. chim.* **40**, 553 (1921); *Chem. Abstracts* **16**, 906 (1922).
- (5) GRIMAUX AND CLOEZ: *Compt. rend.* **110**, 462 (1890).
- (6) HENNINGER: *Ann. chim. phys.* **7**, 213 (1886).
- (7) KRANTZ, J. C., JR., OAKLEY, M., AND CARR, C. J.: *J. Phys. Chem.* **40**, 151 (1936).
- (8) MELLON, M. G., AND NORRIS, V. N.: *Ind. Eng. Chem.* **16**, 123 (1924).
- (9) PICARD, M. P.: *Bull. soc. chim. biol.* **9**, 692 (1927).
- (10) VAN LIEMPT, J. A. M.: *Z. anorg. allgem. Chem.* **3**, 151 (1920).
- (11) WILSON, J. A.: *Ind. Eng. Chem.* **17**, 74 (1925).

NEW BOOKS

Kolloidik. Eine Einführung in die Probleme der modernen Kolloidwissenschaft. By A. v. BUZÁGH. 323 pp. Leipzig: Th. Steinkopff, 1936. Price: unbound, 15 RM; bound, 16.50 RM.

The portmanteau word "Kolloidik" means colloid chemistry and colloid physics; in the language of a century ago, the natural philosophy of colloids. The author is evidently of a philosophical turn of mind, for the whole treatment of the subject is subordinated to his classification of matter according to degree of subdivision primarily and to morphology secondarily. The systematics may become a little tedious to English readers; experimental facts are mentioned strictly in their proper place according to the system of the book. Too often, facts are touched upon only incidentally in the development of the system of classification, and sometimes selection is rather oddly made; thus as functions of dispersity, under the heading "physical," are included transparency, hardness, photoelectric properties (of thin metallic films, which are apparently considered good instances of the effect of thickness on an otherwise homogeneous state of matter, an opinion which the reviewer certainly does not share), and catalysis; as "physicochemical" are mentioned some cases where the ordinary laws of solution or of electrolysis appear, at first sight, not to be obeyed by colloidal systems; and under "chemical," Smekal's theory of the mosaic structure of crystals. Later on in the book the author comes to rather closer grips with the results of experimental research; among many other things dealt with are the results of x-ray investigations into the structure of natural compounds of high molecular weight, liquid crystals, surface films, electrical double layers, the use of electron beams for studying surfaces, sedimentation volumes, theories of adsorption, peptization, swelling, coagulation, etc. But the treatment is rarely sufficiently profound or exact to give the reader a well-balanced idea of the essentials of the phenomena and of their explanation; and literature references are not sufficiently numerous or up-to-date to guide one who wants to master the original literature quickly. It may be that the author has been seriously handicapped by his desire to treat everything logically and systematically from the standpoint of dimensions and manner of aggregation. These are not the fundamental properties of matter; they are sometimes very important and dominate the phenomena, but often they are overshadowed by specific chemical properties, which indeed control them. A natural philosophy of that vast miscellany of phenomena loosely classified as colloids must not forget this; nor indeed is it generally profitable to treat experimental research as a mere handmaid to a subjective scheme of things. The book is tolerably well conceived, but it lacks thoroughness, and shows little originality.

N. K. ADAM.

Reports on Progress in Physics. Published by the Physical Society. Volume II. 25 x 17 cm.; iv + 371 pages. London: The Physical Society, 1936. Price to non-Fellows: 21 s. net.

The second volume of this new venture resembles the first in being printed on excellent paper, with a dignified format and good binding, and in containing a set of reviews written by experts on the theoretical and applied sides, which provides material of the highest interest to physical chemists. The sections are (neglecting

subsections): general physics (Brownian movement, surface tension, viscosity), quantum theory (including theory of valency), atomic physics, geophysical prospecting, radio-exploration of upper atmospheric ionization, sound, heat, electrical and magnetic measurements, the charge on the electron, electron tubes, x-rays (including structures of substances), spectroscopy, and optics. It will be seen that the volume resolutely avoids a narrow view of the subject and overemphasis of certain very new fields. The latter receive proper attention and their due space, but it is rather necessary to emphasize that this report does represent progress in physics rather than in a mere branch of physics, and its value to physical chemists is correspondingly enhanced. The volume is one which every physical chemist should read.

J. R. PARTINGTON.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer 35: Aluminium, Teil A, Lieferung 4. 26 x 17 cm.; pp. x + 535-682. Berlin: Verlag Chemie, 1936. Price: 18 RM.

This part of the volume on aluminum deals with the alloys of aluminum with S, Se, Te, Po, B, C, Si (pp. 536-627), P, As, Sb, Bi, Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba, Ra. The physical properties are given, with tables and curves, and the chemical properties discussed include corrosion. Literature references come to January, 1936. The volume is of particular interest from the chemical engineering point of view and the treatment is thoroughly sound.

J. R. PARTINGTON.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer 55: Uran und Isotope mit einem Anhang über Transurane. 26 x 17 cm.; pp. xviii + 279. Berlin: Verlag Chemie, 1936. Price: 34.50 RM.

The volume on uranium is complete in itself and includes the chemistry of uranium and its isotopes, with a brief account of very recent experiments on the artificial production of elements of atomic number greater than 92 ("Transurane"). There is also a rather brief account of the radioactivity of uranium in which only elements in the series of atomic number 92 are considered, the relation to the actinium series being left rather vague. There is a section on salts of uranium with organic acids. The highly systematized arrangement necessary in a work of this kind has its disadvantages, since there is, for example, no account of uranium X, and uranic acid and uranates are separated, the latter (with other compounds) being included under the various metals. The volume maintains the high standard of the series.

J. R. PARTINGTON.

Stereoscopic Drawings of Crystal Structures. Edited by M. VON LAUE and R. VON MISES; drawings by E. REHBOCK-VERSTÄNDIG; text by G. MENZER. Part 2. 18 x 17 cm.; 56 pp. Berlin: Julius Springer, 1936. Price: in portfolio, 18 RM.

This collection of twenty-four stereoscopic drawings of crystal structures forms a continuation of the series published some years ago by the same authors. In the first volume the structures chosen were those of very simple types; here rather more complicated ones are depicted, although they are still comparatively simple, consisting of those of some of the elements which crystallize in a less regular way than most, and of compounds of two or three elements.

Even for these relatively simple structures the advantages of the stereoscopic method of representation is very considerable. One has only to try first to make out the details of a structure from the drawing without the use of the stereoscope, and

then afterwards to view it stereoscopically to be at once convinced of the immense gain in clarity obtained by so doing. It is a real difficulty in work on crystal structure that the results of an analysis are not easily made clear to the chemist or mineralogist whom they might interest. The ideal method, the study of three-dimensional models, is rarely available, but sets of stereoscopic models of this kind make a very good substitute for models, and one could wish that more of them existed.

Mrs. Rehbock-Verständig has drawn the figures for this volume with much skill, and with the help of the text, which was contributed by Dr. G. Menzer and has been translated into English by Mr. Greenwood, the English and German versions being in parallel columns, it is easy to get a very good idea of the plan according to which the structures here shown are built up. Although, if necessary, this information can be obtained from the *Strukturbericht* of Ewald and Hermann, it would undoubtedly have been a convenience to the reader if references to the sources from which the structures are taken had been given in the text.

R. W. JAMES.

Eclipses of the Sun. By S. A. MITCHELL. Fourth edition, revised and enlarged. New York City: Columbia University Press. Price: \$5.00.

The present, and fourth, edition of this standard treatise on eclipses differs from the previous issues chiefly in the addition of an extra chapter dealing with the recent eclipses of 1932 and 1934. It is unfortunate, in this connection, that at least a few allusions to these eclipses were retained uncorrected from the previous edition. Thus, we find that in 1935 the author still predicts what *will* happen in 1932.

This last chapter contains an excellent summary of some of the conclusions derived from crucial observations made at the occasion of these two recent eclipses, and a description of Lyot's success in obtaining spectra of the corona without an eclipse.

The remainder of the book is still essentially the same as in previous editions, and contains a description of historical eclipses and of the gradual development of and the improvement in the prediction of eclipses; furthermore, some chapters dealing with the working of the spectroscope and giving an outline of our present ideas on the structure of the atom and the theories of ionization and relativity. The remainder of the book is devoted to a detailed description of virtually all well-observed eclipses of modern times from 1842 onward. The arrangement of the chapters suggests that the author had a dual purpose in writing this book, namely, to make it appeal to both professional astronomers and the public at large. The very large amount of personal narrative included was doubtless a concession to the latter, but the reviewer feels that its omission would have made the book more acceptable to the former.

Similarly, in connection with the early historical eclipses a good deal of Egyptian history has been included and a rather invidious comparison made between the astronomical accomplishments of the early Egyptians and the Babylonians, which, in this reviewer's opinion, might well have been left out. Such comparisons represent, at best, only a consensus of opinion rather than a statement of fact, and in the present instance appear to be based chiefly upon the authority of a single egyptologist—Breasted—in a field of such great diversity of opinion.

The reviewer cannot help expressing the wish that the author, one of the foremost observers of eclipses of our times, would condense into a separate monograph all the facts and theories of interest to the professional astronomer, but without any concession to popular appeal in the form of discussions which are, after all, not very relevant from the astronomer's point of view.

W. J. LUYTEN.

Abridged Scientific Publications from the Kodak Research Laboratories. Volume XVI.

Rochester, New York: Eastman Kodak Co., 1935.

This volume contains abbreviated reprints of thirty-four papers which were published from the Kodak Research Laboratories during the years 1933 and 1934. Fifteen of the papers are devoted to subjects more or less closely related to practical photography; six, to the description of scientific apparatus; and the remainder, to a variety of purely scientific subjects. The original papers were published in seventeen different journals, ranging in type from the *Journal of the Society of Motion Picture Engineers* to the *Transactions of the Faraday Society*. The abridged reprints are not mere abstracts, but are sufficiently complete to satisfy the general reader.

ROBERT LIVINGSTON.

Physical Aspects of Organic Chemistry. By WILLIAM A. WATERS, with an introduction by T. Martin Lowry. 14 x 21.5 cm.; xv + 501 pp. New York: D. Van Nostrand Co. Price: \$9.25.

This book deals almost wholly with reactions of organic compounds and only incidentally with problems of structure. Of the seventeen chapters which make up the book, six are concerned with general considerations of the following: chemical affinity, physical theories of molecular structure, valency, electrical dipoles, chemical reactivity, and general polarity. The remaining eleven deal with applications of these considerations to the reactions of organic chemistry.

From the standpoint of physical organic chemistry as a whole this work represents no advance over treatises previously available; but it is of considerable importance as a textbook of the work of the modern English theoretical organic chemists. The author has used their point of view in interpreting the reactions of organic chemistry on an electronic basis. He has rendered a valuable service in collecting and presenting together the most comprehensive, lucid, and convincing body of this sort of material at present available in book form. Typical subjects dealt with from this point of view include: unsaturation, free radicals and their non-ionic reactions, ionization and ionic reactions, acidity, hydrolysis and esterification, molecular rearrangement, aromatic compounds. The arguments in the text are supplemented by abundant literature references. Therefore this should prove an extremely valuable addition to the libraries of those interested in the background of this fast-growing field.

ALBERTO F. THOMPSON, JR.

The Theory of Emulsions and their Technical Treatment. By WILLIAM CLAYTON.

Third edition. vii + 458 pp.; 91 illustrations. London: J. & A. Churchill, Ltd. Price: 25/—.

The third edition of Dr. Clayton's well-known book will be welcomed by all interested in emulsions. It contains very much new material and is twice the size of the second edition, which appeared in 1928. The general arrangement of the book remains much the same, but every section has been greatly enlarged. New chapters include "Emulsifying Agents" (previously a short appendix), "The Preparation of Emulsions—Technical Operations," and "Emulsions in Biological Investigations." References to the recent literature are most complete and up-to-date. Much of the information is not otherwise readily available, this applying in particular to the many facts drawn from the patent literature. Considerable space is given to the new industrial emulsifying agents such as the numerous sulfonated compounds now in use.

The reviewer feels that the theoretical treatment of the subject would have gained considerably in clearness if the method of presentation had been entirely

rearranged, instead of the facts being presented in an order determined by earlier editions.

Dr. Clayton is to be congratulated on producing a volume which will be invaluable to all investigators in this wide field.

C. ROBINSON.

The Nature of Physical Theory. By P. W. BRIDGMAN. Princeton: Princeton University Press, 1936.

In this book the author attempts to analyze critically the basis of physical theory in terms of possible operations (i.e., experimental observations). This operational analysis is applied not only to the several branches of modern physics, but even to such fundamental things as mathematics, logic, and human thought and language. In spite of the rather abstruse character of the subject, the presentation is remarkably clear and the style is simple and vivid.

To many theoretical physicists this book may prove stimulating and perhaps at times provocative. To that larger group who are content to follow the general trend of modern physical theory and occasionally to utilize some of its definite results, it would be illuminating and intensely interesting. The layman should find it helpful in attempting to orient himself in a world of theory which is rapidly changing and sometimes apparently kaleidoscopic. He may also find a few weapons with which he may protect himself from the intellectual arrogance of some of the camp followers of modern physics.

The authors closing words will serve, better than any detailed description, to give the temper of this work; "logic, mathematics, physical theory, are only our inventions for formulating in compact and manageable form what we already know, and like all inventions do not achieve complete success in accomplishing what they were designed to do, much less complete success in fields beyond the scope of the original design, and—our only justification for hoping to penetrate at all into the unknown with these inventions is our past experience that sometimes we have been fortunate enough to be able to push on a short distance by acquired momentum."

ROBERT LIVINGSTON.

Differential Equations in Applied Chemistry. By FRANK LAUREN HITCHCOCK and CLARK SHOVE ROBINSON. Second edition. 120 pp. New York: John Wiley and Sons, Inc., 1936. Price: \$1.50.

The second edition of this excellent little book has been improved by the addition of numerous problems and by the substitution of a treatment of Picard's method of solution of differential equations for the chapter in the first edition which dealt with the graphical evaluation of integral expressions. The six chapters are entitled: Introduction, Processes of the First Order, Processes of the Second Order, Simultaneous Processes, Equations of Flow and the Numerical Solution of Differential Equations. In Chapter V the explanation of the use of Fourier's series has been made much more detailed. This book can be recommended highly to chemists and chemical engineers.

F. H. MACDOUGALL.

Fundamental Experiments in Chemistry. A Handbook for Teachers and Students. By E. D. GODDARD. 19 x 12 cm.; xii + 147 pp. London and Boston: Ginn and Co., Ltd., no date. Price: 3s. 6d. net.

Although this book is primarily intended for chemistry teachers in schools and admirably fulfils its purpose in this field, it is noteworthy for the very detailed instructions it gives for assembling and performing some of the fundamental experi-

ments relating to the composition of gases (water, hydrogen chloride, ammonia, carbon dioxide, carbon monoxide, nitrous and nitric oxides, and ozone) usually shown in lecture demonstrations, so that it would be a very useful book to have in the preparation room of a college chemistry department. In many cases such experiments fail for want of attention to some minor point, and Mr. Goddard's book will usually disclose this point. The details of apparatus are given, and the book may be strongly recommended. Teaching hints will be found useful in schools.

J. R. PARTINGTON.

Kurzgeschichte der Chemie. By F. FERCHL and A. SÜSSENGUTH. 26 x 19 cm.; 230 pp.; 200 illustrations. Mittenwald (Bavaria): A. Nemayer, 1936. Price: unbound, 12 RM.; bound, 15 RM. (less 25 per cent).

This book is a noteworthy supplement to all existing histories of chemistry in that it is mostly illustrative material. There is a satisfactory amount of text, and this takes account of recent studies in the subject, some of which have considerably modified older ideas. The illustrations are reproductions from actual manuscripts, old books, etc., and are very attractively printed on art paper with explanatory legends. The reviewer found the book absorbingly interesting, and he is sure that his colleagues will like to share his pleasure. There are many portraits of famous chemists, some unusual and some (e.g., of Libavius) rarely seen, and some illustrations of old laboratory interiors. One of the authors is Director of the Chemical Section of the Deutsches Museum, Munich, and has had unusual facilities for collecting material.

J. R. PARTINGTON.

Tables of Physical and Chemical Constants and some Mathematical Functions. By G. W. C. KAYE and T. H. LABY. Eighth edition. 25 x 16 cm.; 162 pp. London: Longmans, Green and Co., 1936. Price: 14 s. net.

Kaye and Laby's is the best known short book of tables. The fact that it has reached eight editions since its first publication in 1911 is proof that it fills a need. It is one which the individual worker can afford and find space for in his laboratory, the larger volumes of tables finding a place in the library. The revision has been successfully extended to several parts, but there are still some old values which there is no point in retaining. Hartmann's values for the ratios of specific heats of gases (p. 61) are worthless and might have been replaced; the book by Partington and Shilling is now available for reference here. Only very old values for the dielectric constants of gases are given on p. 88; some of the historical data on p. 1 is incorrect; the English silver coin has long ceased to have the composition attributed to it on p. 22; and the melting point of chlorine dioxide on p. 120 appears to be copied from the Landolt-Börnstein *Tabellen* and, as it is really in Fahrenheit degrees, is incorrect as it stands. These are examples of what the editors and their helpers should not have missed in their eighth edition. In future editions—which should be thoroughly overhauled—it would be better to send each section to specialists for comment. It could then become a really valuable book. As it is, no worker can safely rely on any figure unless he has also looked up the recent literature.

J. R. PARTINGTON.

Recent Advances in Organic Chemistry. Volume II. By A. W. STEWART, with four new chapters by H. GRAHAM. 22 x 14 cm.; xiv + 489 pp. London: Longmans, Green and Co., 1936. Price: 21 s.

This is in the main a re-issue of the 1931 edition, but the four chapters by Dr. Graham are new and deal with such interesting and important topics as the bile

acids and sterols, the cardiac aglucones, hormones, and vitamins. These chapters give the reader an excellent idea of the subjects mentioned, and constitute a valuable addition to the book. They bring the subjects as nearly up-to-date as could reasonably be expected.

With regard to the rest of the volume, this is, as ever, stimulating. It must surely induce enthusiasm in at any rate a few of those who come relatively fresh to the subject. It is a pity that the author appears to favor the views of certain schools to the exclusion of those of others whose contributions are quite as outstanding. For example, in the chapter entitled "Some Applications of Electronics," one finds no mention of either Ingold or Sidgwick, and Robinson is named only once. This same chapter gives the reader the idea (p. 373) that our knowledge of activation within aromatic systems has not advanced appreciably in the last thirty years. The chapter called "Some Unsolved Problems" deals with some slight questions to the exclusion of others of much greater profundity: the Wagner-Meerwein theory is not mentioned in that section which refers to the problem of the pinacol-pinacolin and similar changes, and a stereochemically improbable formula for diacetylacetone is given credence.

In the chapter dealing with "The Diphenyl Problem," the reader must remember that the "Recent Advances" are those before 1931. This particular problem is presented in a straightforward manner, although more could have been achieved in the space actually taken.

E. E. TURNER.

Physical Chemistry. By FRANK H. MACDOUGALL. 15 x 22 cm.; ix + 721 pp.; 97 figs. New York: The Macmillan Co., 1936. Price: \$4.00.

If one were to judge this book only by an examination of the table of contents and by a brief perusal of its pages, he might be led to believe that it is only the Macmillan Company's competing book in a field which seems already well-supplied with text books. With a more thorough examination of its contents and of the author's style of presentation, it becomes apparent that Professor MacDougall has accomplished something very worth while in the teaching of physical chemistry.

The arrangement of the material is quite orthodox except that a short chapter (Chapter II) appears early on energy and the first law of thermodynamics, as does his consideration of the structure of atoms (Chapters VI and VII). As the author says in his preface, "it is generally recognized nowadays that an adequate introduction to the science of physical chemistry must offer the student the opportunity of becoming acquainted with the elements of thermodynamics and with the more important thermodynamic relations." This opportunity is given in this book in a most thorough and rigorous way. To one who has not offered such material in a course in elementary physical chemistry it may seem to present too much difficulty for the average student, yet the treatment is so detailed and straightforward that this difficulty has been reduced to its minimum.

The author makes a point of his treatment of electromotive forces and potential differences, and his treatment of this subject is again characterized by both rigor and clarity of thought and expression.

Beginning with Boltzmann's theorem and Poisson's equation he gives a derivation of the Debye equation for the activity coefficient of strong electrolytes. This the author admits is beyond the beginning student in physical chemistry, but he includes it in the hope that it may be useful in later reference. There is so much material in its seven hundred-odd pages that some omissions would in any event be made. On the whole the text seems to be an excellent one, and there is every reason to believe that it will be enthusiastically received.

T. R. HOGNESS.

Elementary Principles in Physical Chemistry. By T. J. WEBB. 16 x 23 cm.; x + 344 pp.; 25 figs. New York: D. Appleton Century Co., 1936. Price: \$4.00.

In the preface the author states that this book was written for junior and senior students who have had preliminary training in the descriptive phases of chemistry, in general physics, and in the calculus. It takes no more than a general perusal of the contents to realize that he has written for the superior student who is to specialize in some field of chemistry.

The book differs from most texts in this field in that it is somewhat more advanced. Some of the theorems which are usually mentioned in an already developed form are developed in considerable detail, such as the Debye-Hückel limiting law of strong electrolytes, which includes a development of Poisson's equation, the Schroedinger equation, reaction velocities from the configuration-potential energy standpoint of Eyring, the quantum theory of the rotator and oscillator, and many theorems in thermodynamics. Most students taking an elementary course in physical chemistry are not sufficiently prepared for some of these considerations.

"The content of the book revolves about the two fundamental problems of theoretical chemistry, viz., the state of equilibrium in a chemical reaction and the rate at which the state of equilibrium is attained." Consequently, very little consideration is given to the physical properties of the liquid and solid state. For example, there is no discussion of the subjects of surface tension and dielectric constants. The book is replete with formulae and derivations and contains a relatively small amount of factual and descriptive material.

This should be an excellent text for the more advanced student in physical chemistry. If the student's only contact with physical chemistry is to be in a course in which this book is used as a text, a good deal of supplementary work on the part of the instructor will be necessary. However, during some time in his training the student in physical chemistry should become acquainted with those subjects the treatment of which distinguishes this book from those which have already appeared.

T. R. HOGNESS.

AN ELECTRONIC ANALYSIS OF SOME SURFACES BY MEANS OF SLOW ELECTRONS¹

ROBERT J. MOON AND WILLIAM D. HARKINS

Department of Chemistry, University of Chicago, Chicago, Illinois

Received June 11, 1936

INTRODUCTION

Much of our knowledge of matter is that of its surface. It is fortunate that we have such information concerning surfaces, for many different types of physical and chemical phenomena are quite dependent upon the nature of the surface. For example, the absorption and emission of heat and light, thermionic emission, secondary electron and photoelectron emission, contact potentials, surface tension, rate of a chemical reaction, catalysis, adsorption, friction and so forth are dependent upon the condition of one or more surfaces. A surface may be thought of as consisting of atoms or molecules distributed at random, or in some orderly fashion. The interaction of waves with a regularly arranged network of matter produces reflected waves, which combine in such a way that, from their space intensity distribution recorded at a distance from the network, some dimensions of the network may be calculated. Electron waves are now a reality and have become a useful tool in studying atomic and molecular networks found at and near the surface.

Since the discovery of the wave characteristics of electron beams by Davisson and Germer (2) many workers have used electron waves to investigate films and surfaces of crystalline solids. Some organic liquids have been studied (1, 3).

Slow electron waves have the least penetrating power of any radiation which exhibits a wave nature, therefore they are quite sensitive to surface layers. Low velocity electrons probably never penetrate more than ten atom layers. The major part of the diffraction of the electron wave by metals occurs in the first two layers.² Slow electrons are quite suitable for the study of surfaces which consist of only a few molecular layers.

¹ Presented before the Thirteenth Colloid Symposium, held at St. Louis, Missouri, June 11-13, 1936.

² "A known number of atom layers of one metal were deposited on the surface of a single crystal of another metal by evaporation in high vacuum. Direct results on depth of penetration were obtained from measurements on electron diffraction as a function of the thickness of the surface layer. A silver film deposited on a copper crystal is amorphous. A layer one atom deep reduces the maxima of the beams from

THEORETICAL DISCUSSION

An electron beam incident on a surface makes an angle θ with the surface. In order to measure distances normal to the surface by means of diffracting electron waves, the condition that the angle of incidence equal the angle of reflection must be satisfied, and this may be met by having the collector receive only those electrons reflected at an angle equal to the angle of incidence. If the surface is composed of atoms lying in planes spaced at a distance d , measured normal to the surface, and the Bragg condition

$$n\lambda = 2d \sin \theta \quad (1)$$

is satisfied, electron waves reinforce each other and a maximum collector current results. Here λ is the wave length of the electron wave as given by the de Broglie relation

$$\lambda = h/mv \text{ centimeters} \quad (2)$$

where h is Plank's constant, m is the mass of the electron, and v is the velocity of the electron. In turn, v is given by

$$v = (2Ve/m)^{\frac{1}{2}} \quad (3)$$

where V is the accelerating potential in absolute E.S.U., and e is the charge on the electron in absolute E.S.U. Substitution of this in equation 2 gives

$$\lambda = \frac{12.214 \times 10^{-8} \text{ cm.}}{(P)^{\frac{1}{2}}} \quad (4)$$

where P is the accelerating potential measured in practical volts. Substitution of equation 4 in equation 1 gives

$$P^{\frac{1}{2}} \sin \theta = 6.107 \times n/d \quad (5)$$

which is the condition that is satisfied for maximum collector current. This relation assumes no inner potential.

For a given surface having zero inner potential the condition for maximum collector current is $P^{\frac{1}{2}} = \text{constant} \times n$. If two maxima are chosen with quite a few others existing between, ordering of the maximum may be readily accomplished. For

$$P_1^{\frac{1}{2}}/P_2^{\frac{1}{2}} = n_1/n_2$$

the copper lattice by at least seventy per cent for energies up to 300 electron volts. A number of foreign silver atoms equal to a few hundredths of that contained in one atomic layer can be detected by this method. A silver film deposited on a gold crystal is crystalline. The surface atomic layer of silver contributes at least ninety per cent. This predominating effect of surface atomic layers for primary energies as high as 300 electron volts is not in accord with the theoretical predictions of v. Laue." (Farnsworth, H. E.: Phys. Rev. 47, 331A (1935).)

where P_1 is the voltage where maximum of the order n_1 occurs, and P_2 is the voltage for maximum n_2 . Now $n_2 = n_1 + a$, where a is the number of maxima existing in going from n_1 to n_2 . Substitution for n_2 and rearranging gives

$$n_1 = a \frac{P_1^{\frac{1}{2}}}{P_2^{\frac{1}{2}}} - P_1^{\frac{1}{2}} \quad (6)$$

from which the order n_1 may be found.

The more general cases of diffraction of electrons must take into account the so-called inner potential, ϕ . The velocity of the electron wave within the lattice will be different from the velocity of the electron wave just outside the lattice, if the inner potential is different from zero. The ratio of these velocities, or in other words the index of refraction, μ , is given by

$$\mu = \left(1 + \frac{\phi}{P}\right)^{\frac{1}{2}} \quad (7)$$

and the maxima should obey

$$P^{\frac{1}{2}} \sin \theta = 6.107 \frac{n}{d} \left(1 - \frac{4d^2\phi}{150n^2}\right)^{\frac{1}{2}} \quad (8)$$

APPARATUS

An electron diffraction apparatus (figure 1) was constructed which has the following features: (1) The specimen holder remains in a fixed plane. (2) The specimen holder may be quickly removed, and replaced when changing specimens. (3) The collector and electron gun can be simultaneously rotated in such a way as to satisfy the condition that the angle of incidence equal the angle of reflection. (4) The filament of the electron gun may be renewed through a side tube. (5) The entire apparatus is constructed of brass to avoid contact potentials.

The electron beam is produced by means of an electron gun (G), and is collimated by means of three thin circular apertures (S_1, S_2, S_3) 0.55 mm. in diameter. The entire slit system is mounted upon arm A_1 , and may be adjusted by the two screws (V) for alignment. The collar (W) holds the filament system in the correct position, and may be removed when spot-welding a renewal filament, which consists of three turns of 0.005-in. tungsten wire forming a spiral 1 mm. in diameter. It is spot-welded onto two 0.040-in. nickel wire leads. The axis of the spiral is coaxial with the slit system. The filament spiral is 1 mm. from the first aperture (S_1). The nickel leads are supported by means of a lavite insulator. A copper strip $\frac{5}{8}$ in. long, $\frac{1}{16}$ in. wide, and $\frac{1}{32}$ in. thick, bent in the middle to form a split connector, is silver-soldered to each end of the nickel wire leads, and these connectors are held by means of two lavite blocks, the upper one of

which has a brass screw (L) attached to it which passes through the hexagonal nut held by means of a shoulder in the brass case. Pressure is applied on the copper contacts when the nut is turned in a counter-clockwise direction, so that the two brass tips may be clamped in the copper connectors. These brass tips are mounted in a lavite block, which is supported on the shield K, which has a bearing in the center of the shaft connected to the electron gun arm and carries two flexible copper conductors, which consist of seventy-two strands of 0.005-in. wire, insulated from the shield by means of glass beads. The upper conductors are silver-soldered to the brass tips. The shield has a small rack attached to it

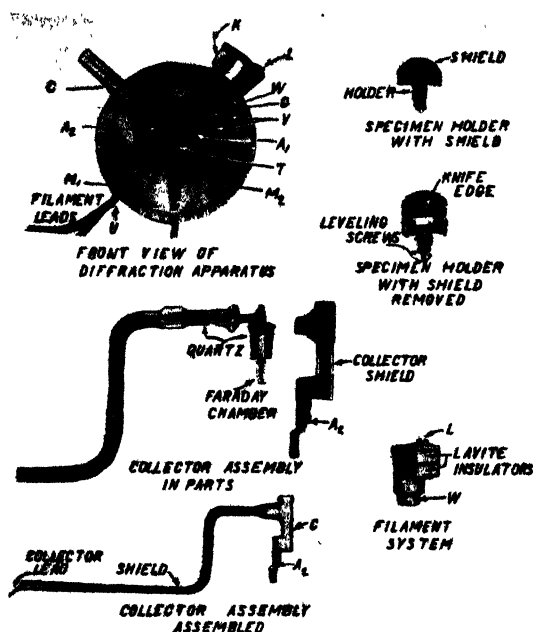


Fig. 1. Electron diffraction apparatus

which enables the brass tips to be slipped from between the copper connectors by means of a tool containing a small pinion gear, which centers on the brass nut. The filament assembly can be removed through a side tube when the brass tips are in this position. A small spring catch either holds the brass tips in between the connectors, or holds them away. The copper tubes (U) shield the filament leads up to the point at which they leave the glass enclosure. Shielding outside the enclosure is effected by means of a braided copper sheath.

The collector (C) consisted of a small Faraday chamber held in place by a quartz insulator behind the 0.55-mm. aperture, which is mounted on the

arm (A_2). The lead to the collector is brought through a quartz tube (6 mm. outside diameter, 3 mm. inside diameter), and it is bent so that the electrometer lead leaves the quartz insulator coaxial with the mechanism used to rotate the collector and gun. A braided copper shield over the

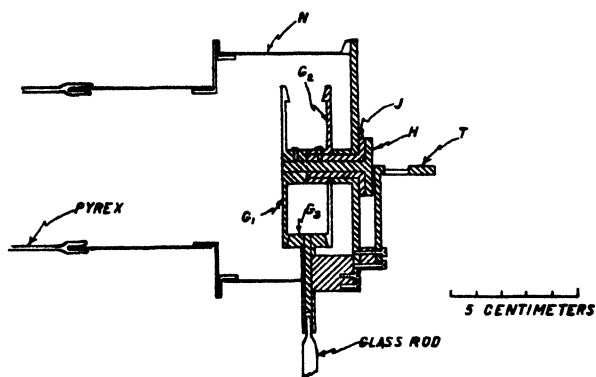


FIG. 2. Gearing mechanism

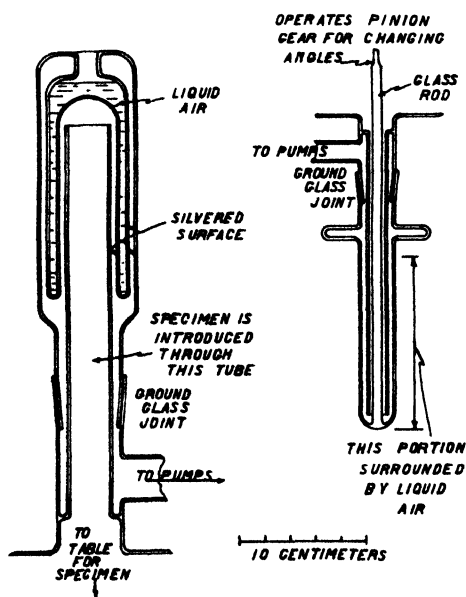


FIG. 3. Grease traps

quartz serves for electrostatic shielding for the electrometer lead within the glass enclosure.

The arm of the electron gun is fastened rigidly to the shaft H (figure 2), which is, in turn, fastened rigidly to the gear G. The collector arm is fastened rigidly to the shaft J, which is fastened to the gear G_2 by means of three

set screws. Motion in opposite directions is imparted to the gears G_1 , G_2 by the small gear G_3 . The three set screws on the large gear (G_1) allow adjustment of the collector, so that the angle of incidence equals the angle of reflection. The angles are read from the scale engraved on the base plate by the two indexes (M_1 , M_2) connected to the electron gun and collector, respectively. The base plate is mounted on the large copper tube N, which is mounted on a smaller copper tube ($2\frac{1}{2}$ in. in diameter) by a slotted flange. The other end of the smaller tube is sealed directly to the Pyrex glass.

The table T, mounted on the base plate, is adjustable for alignment. It has a milled channel to receive the specimen holder. The specimen is mounted on a circular table in the specimen holder. This table is held against three leveling screws by a tungsten spring.

A shield constructed of two semicircular pieces could be mounted upon the specimen holder to shield the electron beam from any electric field which might be created by charges accumulating on the glass wall of the enclosure approximately 76 mm. from the specimen. A 10° wedge placed between the two semicircular pieces with its knife edge 0.5 mm. from the specimen could be used to separate the incident electron beam from the diffracted beam.

It was necessary to use ground glass joints lubricated with stopcock grease on the control for changing the angle and on the tube through which the specimen is introduced into the apparatus. It is equally necessary to keep the stopcock grease from the surface of the specimen. Figure 3 illustrates the method used to prevent stopcock grease from entering the apparatus proper.

THE ELECTRICAL CIRCUIT (FIGURE 4)

The filament of the electron gun is heated by the battery (B_1 , figure 4) and the filament heating is controlled by rheostat R_1 , which gives a coarse adjustment, and by rheostat R_2 , which gives a fine adjustment. The accelerating voltage is supplied from a 1000-volt lead storage battery (B_{A1}) in steps of 100 volts. Intermediate accelerating voltages are obtained by means of the potentiometer R_4 and the 50-volt auxiliary battery (B_{A2}). The accelerating voltage is measured by the potentiometer P and the volt-box R_3 through switches Q_2 and Q_3 .

The collector current is measured with the Dershem electrometer (E). The electrometer leak (R_5) of 2.56×10^{11} ohms was not used in all of the experiments. The electrometer sensitivity control employed the following resistances: $R_6 = 80,000$ ohms; $R_7 = 2,000$ ohms; $R_8 = 80,000$ ohms; and R_9 , which consisted of two variable resistances of 50,000 ohms and 1,000 ohms connected in series. The electrometer sensitivity was checked

throughout an experiment by the potentiometer P, through the grounding key Q_1 and the switches Q_2 and Q_4 .

In some of the experiments a constant retarding potential was applied to the collector by introducing a battery between points a and b. In later experiments apertures S_4 and S_5 , 1 mm. in diameter, were added to the collector, and S_6 was enlarged to 1 mm. in diameter. The retarding potential was then applied between the aperture S_4 and S_5 and was equal to the accelerating potential minus the potential from battery B_2 . If vacuum conditions were poor, positive ions would form around S_6 , com-

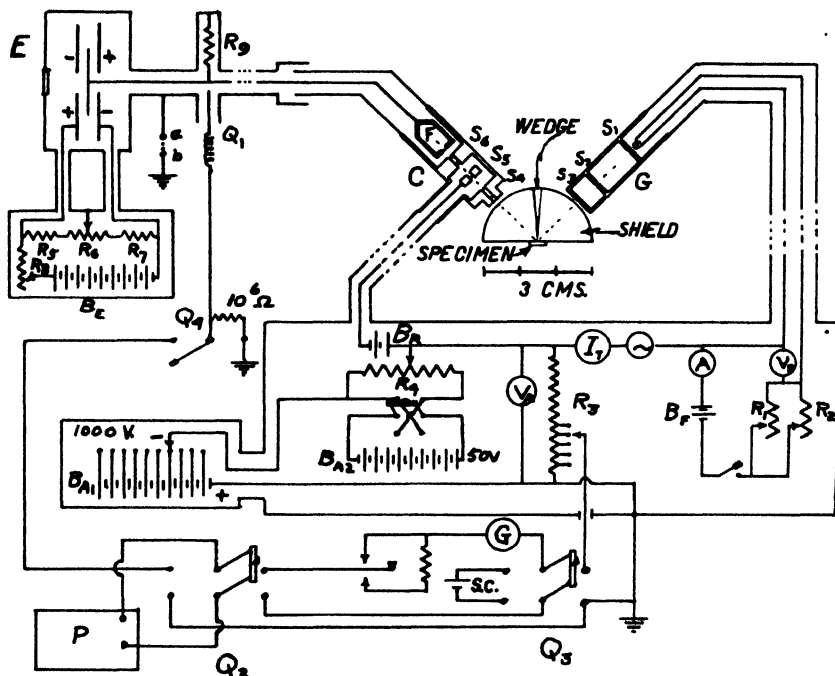


FIG. 4. Electrical circuit

pletely shielding it from the electron beam, and in order to stop electrons from entering the collector, it was necessary to make S_6 several volts (35 volts in some cases) more negative than the electron gun filament.

All parts of the diffraction apparatus, with the exception of the electron gun filament, aperture S_6 , and the Faraday chamber, were at ground potential.

MEASUREMENTS

Diffraction of electrons from oleic acid

Some of Kahlbaum's technical oleic acid, which had been further purified by evaporation in a vacuum at an extremely slow rate, was first investi-

gated. The drift-rate method³ was used to measure the collector current. The filament heating current was kept constant, and the thermionic emission was read for each accelerating voltage. The electron beam was interrupted between measurements.

Experiment with a fixed angle of $7^{\circ}30'$. The values of i_c/i_t (collector current/thermionic current) in arbitrary units are plotted as the ordinate, and values of $P_a^{1/2}$ (square root of accelerating voltage) in units of (practical volts)^{1/2} are plotted as the abscissa in figure 5. Data for the curve follows a sequence in voltage from *A* to *B*, then *C* to *D*, and then *E* to *F*. The data form a smooth curve from *A* to *B*. Curves *CD* and *EF* are displaced, owing to the large jumps in voltage from *BC* and *D* to *E*. It is noted that

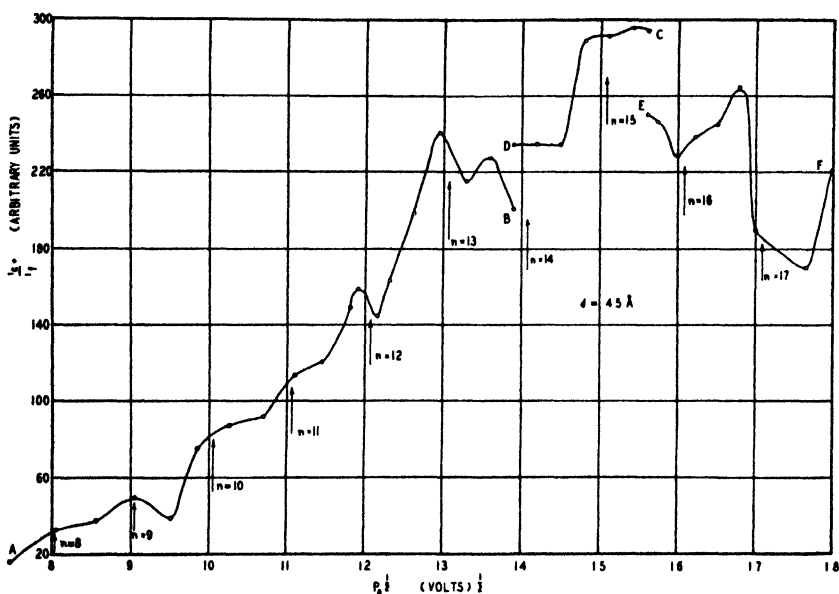


FIG. 5. Diffraction of electrons from oleic acid. $\theta = 7^{\circ}30'$

the change in intensity (i_c/i_t) is greater for the jump *B* to *C* than for the jump *D* to *E*. Many workers⁴ in electron diffraction have found reduction in intensity with continued bombardment with electrons, and have classified it as a "fatigue effect," possibly due to a growing surface charge. The effect above, however, is found when a large change in voltage is made, and might be classed as a fatigue effect in view of the fact that, if a period of half an hour is allowed to elapse, the erratic points return to normal values.

³ The time required for drifting between two fixed points 20 mm. apart on the electrometer scale was measured. The current is inversely proportional to this time. The electrometer sensitivity was 500 mm. per volt.

⁴ G. P. Thomson. Emslie, Rupp, Dames, and others.

In ordering the maxima it was assumed that the maxima in the curve from A to B belonged to the same spacing distance, and that the inner potential was zero. A maximum exists at $P_1^\dagger = 8.03$ volts[†], and another at $P_2^\dagger = 13.1$ volts[†]. There are five maxima ($a = 5$) in going from n_1 to n_2 . Substitution in equation 6 gives $n_1 =$ approximately 8, as n must be a whole number. Substitution of these orders in the Bragg equation gives

$$d = 44.9 \text{ A.U.}$$

Table 1 gives the various values of P^\dagger as calculated for $d = 44.9$ A.U. and the observed values of P^\dagger .

The arrows in figure 5 indicate the positions of the calculated maxima. The calculated positions for the fourteenth and sixteenth orders are misfits.

TABLE 1
Calculated and observed values of P^\dagger

ORDER	P^\dagger (CALCULATED)	P^\dagger (OBSERVED)
8	8.03	8.03 ± 0.05
9	9.04	9.05
10	10.04	10.05
11	11.05	11.05
12	12.05	11.95
13	13.06	12.95
14	14.07	13.6
15	15.08	Insufficient data
16	16.08	16.0 (minima)
17	17.09	16.8
18	18.09	Insufficient data

Experiments with a fixed angle of 30° . These data exhibit three rather broad maxima (figure 6). The best fit for these maxima corresponds to a spacing distance of 3.2 A.U. for the second, third, and fourth orders. This distance is considerably less than the 4.8 A.U. for oleic acid, which was found by Sogani (5) by diffraction of x-rays. However, Sogani's values are, for the most part, large. There are several minor peaks on the broad ones, which are outside of the experimental error. These might be assigned to the very large spacing found in the previous experiment. For a spacing of 45 A.U., ΔP^\dagger should have a value of 0.271 volts[†]. On examining the curve, several peaks are found which might belong to this spacing. However, for $P_a^\dagger = 10$, the order is 43 and the intensity of these peaks is expected to be extremely weak.

The values on the curve were taken in the following order: from a to b ; then the single point c ; then d to e . Point c is far below the curve. The curve d to e was affected very little, if any, by the jump to point c , as only

a single reading was taken there and it required a bombarding time of sixty-five seconds. This would seem to indicate that the charging up of the surface (if that is the case) requires a greater time than one minute.

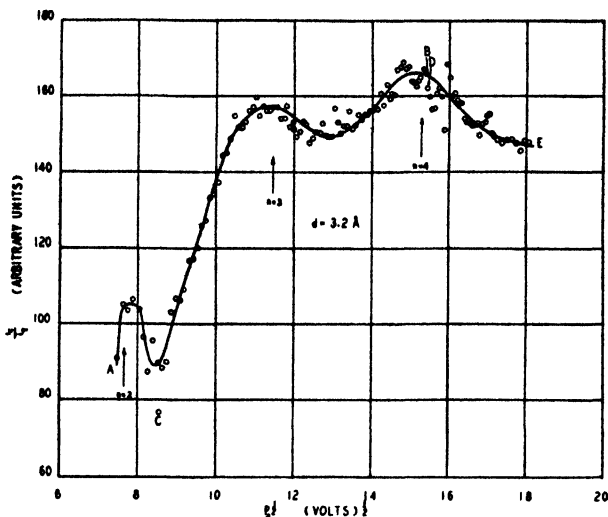


FIG. 6. Diffraction of electrons from oleic acid. $\theta = 30^\circ$

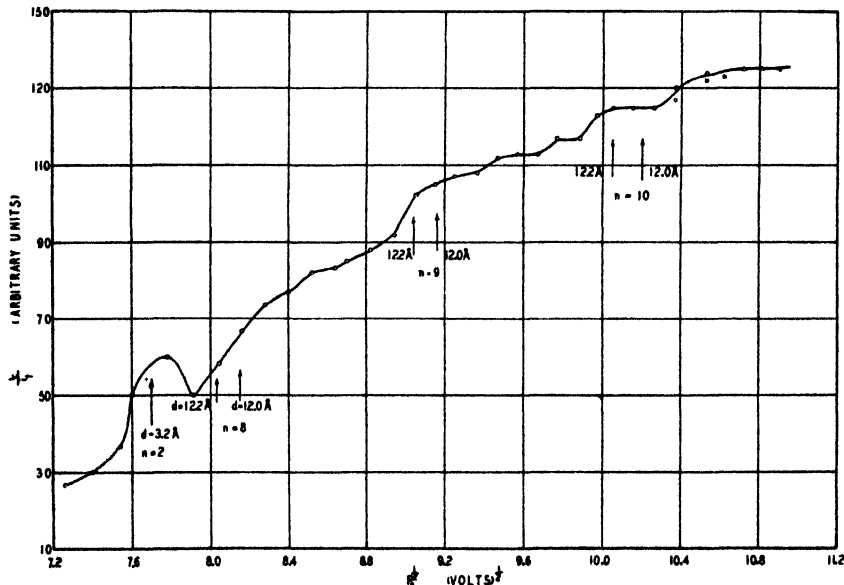


FIG. 7. Diffraction of electrons from repurified oleic acid. $\theta = 30^\circ$

A portion of the sample of oleic acid used above was further purified by evaporation *in vacuo* at an even slower rate than previously. This proc-

ess removed a very small percentage of solid acids. An experiment (figure 7) was made on this sample for the region from $P^{\frac{1}{2}} = 7$ volts[†] to $P^{\frac{1}{2}} = 11$ volts[†]. The collector current was measured by taking the potential drop across a resistance of 2.56×10^{11} ohms by means of the electrometer. The thermionic current was kept at a fixed value by adjusting the filament current. A maximum, which corresponds to the second order for $d = 3.2$ A.U., is quite pronounced. This experiment, as well as all the others on oleic acid, failed to show good evidence for the distance of 12.0 A.U. as reported by Buhl and Rupp (1). The positions for the maxima corresponding to the eighth, ninth, and tenth orders for a spacing of 12 A.U. are indicated in figure 7.

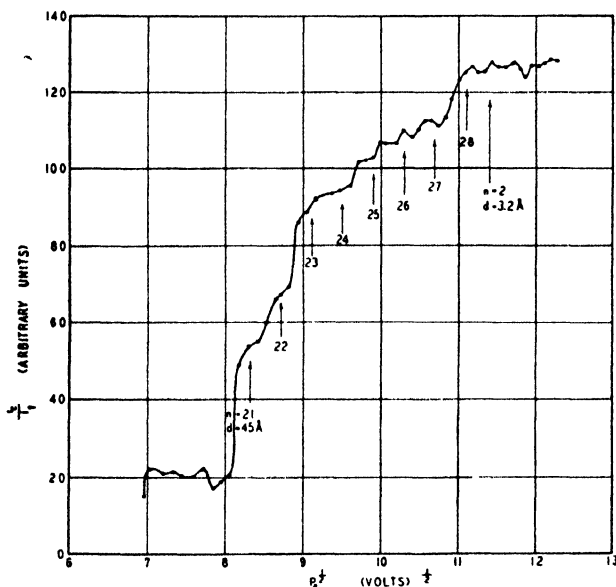


FIG. 8. Diffraction of electrons from oleic acid. $\theta = 20^\circ$

Experiment with a fixed angle of 20° (oleic acid). The angle used in this experiment was such that the maxima for the 3.2 A.U. spacing were too broad ($P_a^{\frac{1}{2}} = 5.7$ volts[†]), and the maxima for the 45 A.U. spacing were of high orders. The second order for a spacing of 3.2 A.U. and the twenty-first to the twenty-eighth order for a spacing of 45 A.U. are indicated by arrows on the graph for comparison (figure 8).

Diffraction of electrons from the (100) cleavage plane of a single crystal of sodium chloride

Large single crystals of sodium chloride were cleaved in order to obtain a fresh surface. The size of the crystal thus prepared was about 5 mm. x 5 mm. x 3 mm. The crystal was put on the holder and placed in the

apparatus, and evacuation was begun at once. The diffracting surface was the (100) plane. The azimuthal orientation of the crystal was such that the (010) planes were parallel to the plane of the incident electron beam and the normal to the (100) plane at the point of incidence. In these experiments the filament heating current was kept constant. The collector current passed through a resistance of 2.56×10^{11} ohms and was measured with an electrometer, which registered the potential drop it created. The period of the electrometer under such conditions was approximately sixty seconds. The surface was bombarded with electrons for equal time intervals for each reading. The electrometer sensitivity

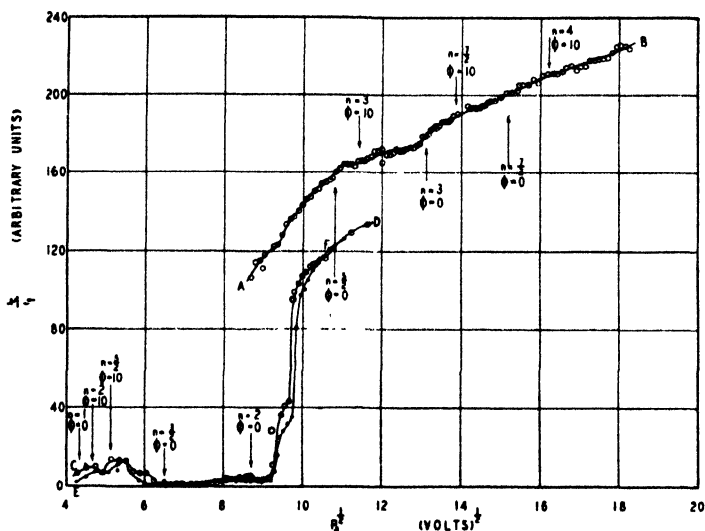


FIG. 9. Diffraction of electrons from the (100) cleavage plane of a single crystal of sodium chloride. $\theta = 30^\circ$

was 500 divisions per volt. A retarding potential of 4.5 volts, applied to the collector, was used in the experiments with sodium chloride.

Experiment 1, curve AB of figure 9 ($\theta = 30^\circ$). Curve AB is a plot of the collector current against $P_a^{\frac{1}{2}}$. The surface of the sodium chloride crystal was bombarded with electrons for a period of sixty seconds at each voltage, and bombarding was discontinued for a period of ten to twenty seconds while the voltage was changed. Curve AB exhibits a broad maximum, which fits both the third order with an inner potential of 10 volts (4, 6), and the $5/2$ order with an inner potential of zero. A second rather weak maximum corresponds to the $7/2$ order with an inner potential of 10 volts, and the third order with an inner potential of zero. Four possible maxima ($n = 3, \phi = 0$; $n = 7/2, \phi = 10$; $n = 7/2, \phi = 0$; $n = 4$,

$\phi = 10$) would occur in the region from $P_{\frac{1}{2}}^{\frac{1}{2}} = 13$ volts $^{\frac{1}{2}}$ to $P_{\frac{1}{2}}^{\frac{1}{2}} = 16.2$ volts $^{\frac{1}{2}}$. This might explain why there are no well-defined maxima in this region.

Experiment 2, curve CD of figure 9 ($\theta = 30^\circ$). The filament was allowed to burn for two hours before any data were taken. A well-defined maximum occurs corresponding to the second order for $n = 5/2$ and $\phi = 10$. This maximum exhibited a fluctuating intensity, though the average collector current was fairly constant. The encircled points on the curve are check points taken at the end of the experiment. The agreement is excellent.

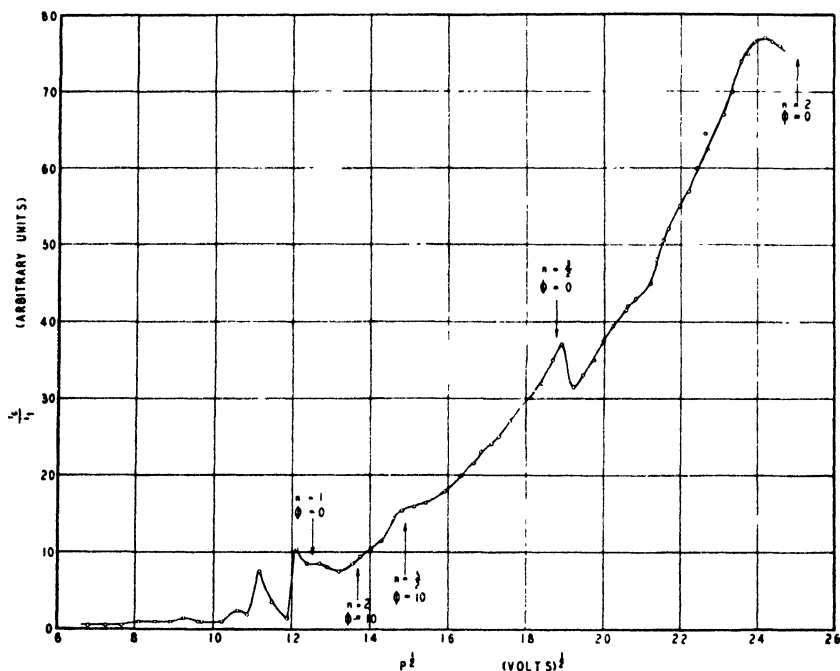


FIG. 10. Diffraction of electrons from the (100) cleavage plane of a single crystal of sodium chloride. $\theta = 10^\circ$

Experiment 3, curve EF of figure 9 ($\theta = 30^\circ$). The surface was bombarded for a period of ten seconds with 386-volt electrons. A period of fifty seconds was allowed to elapse before a reading which required sixty seconds to complete was taken. This curve shows fair agreement with curve CD. In addition to the maxima exhibited in curve CD, curve EF has two other rather weak peaks, which correspond to $n = 3/2$ and $\phi = 0$, and $n = 2$ and $\phi = 0$. Peaks corresponding to a lattice potential of zero are often weaker than the regular peaks for a great many substances.

The values $d = 2.81$ A.U., $\theta = 30^\circ$, and $\phi = 10$ volts were substituted in equation 8, which yielded the condition for maxima

$$P^{\frac{1}{2}} = 4.34 (n^2 - 2.106)^{\frac{1}{2}}$$

$P^{\frac{1}{2}}$ for the maxima, which correspond to $n = \frac{1}{2}$ and $n = 1$, has an imaginary value and the maxima should be absent.

Experiment 4, sodium chloride, figure 10 ($\theta = 10^\circ$). A retarding potential equal to 6 volts less than the accelerating potential was applied between the apertures S_4 and S_5 . Electrons which had lost 6 volts or more of their original energy did not enter the Faraday chamber. The curve exhibits four maxima, three of which agree best with $n = 1$, $n = 3/2$, and $n = 2$ for $\phi = 0$. The calculated and observed maxima are given in table 2.

The diffraction of electrons from the (100) cleavage plane of galena at 206°C.

A large single crystal of natural galena was cleaved into a smaller crystal (3 mm. x 3 mm. x 2 mm.). The (100) plane thus obtained appeared

TABLE 2
Calculated and observed values of $P^{\frac{1}{2}}$

n	$P^{\frac{1}{2}}$ (CALCULATED)	$P^{\frac{1}{2}}$ (OBSERVED)
1	12.52	11.2
3/2	18.78	12.1
2	25.04	18.9
		24.2

quite uniform to the eye by reflected light. Preliminary measurements on this crystal at room temperature failed to reveal any clearly defined peaks between 50 and 420 volts.⁵ The furnaces used for degassing the apparatus were put in place and the entire apparatus was heated to 200°C. for seven days. At the end of that time the pressure in the apparatus was 7.0×10^{-6} mm. with the usual heating current passing through the filament. Nine maxima were found between 50 and 300 volts, with the angle of incidence equal to 75° . It was impossible to use retarding potential in this experiment, as the dielectric absorption current in the quartz insula-

⁵ The previous experiments on sodium chloride gave maxima which were relatively weak in intensity. Laschkarew (Z. Physik 85, 631 (1933)) and his coworkers found that a single crystal of graphite acted as an electron optical surface at room temperature. That is, the collector current exhibited no maxima or minima as the accelerating voltage was varied. However, upon heating the crystal for two hours at 200°C. and then making observations at that temperature, very intense maxima were found. They explained this as being due to the ability of the graphite to absorb gas at room temperature and inability to retain it at 200°C.

tion on the collector system required too long a time to reach equilibrium. The thermionic current was kept constant at 0.500 milliampere by adjusting the filament heating current with a variable carbon resistor. The electrometer leak was 2.56×10^{11} ohms, and the electrometer sensitivity was 250 divisions per volt.

TABLE 3

Experiments on galena with different cooling agents on the grease traps

DATE OF EXPERIMENT	CURVE IN FIGURE 9	COOLING AGENT ON GREASE TRAPS	COOLING AGENT ON OTHER TRAPS
August 7, 1935	AB	Crushed carbon dioxide in acetone	Liquid nitrogen
August 10, 1935	CD	None	Liquid nitrogen
August 11, 1935	EF	Liquid nitrogen	Liquid nitrogen

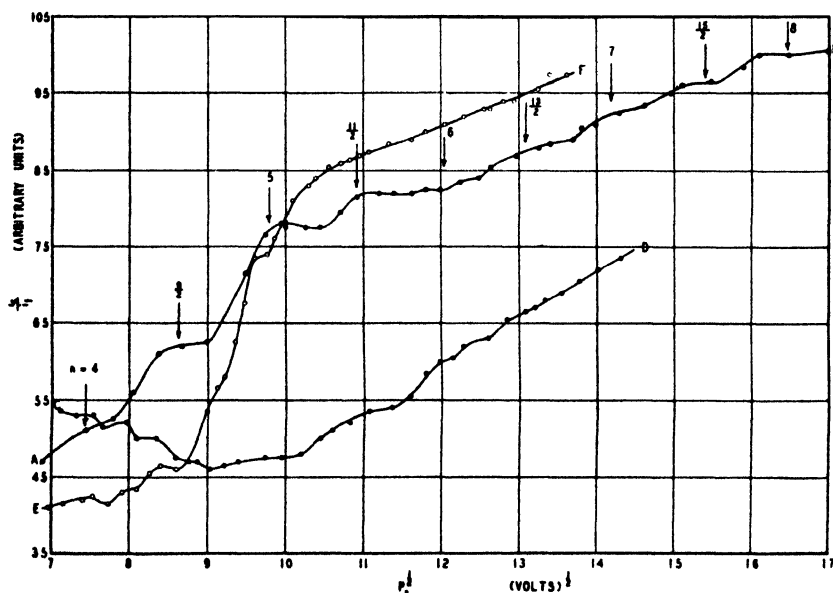


FIG. 11. Diffraction of electrons from the (100) cleavage plane of galena at 206°C .
 $\theta = 75^{\circ}$; $\Phi = 16.9$ volts

All of the following experiments on galena were performed with the entire diffraction apparatus at approximately 206°C . The experiments differed only in the cooling agent used on the traps, as shown in table 3.

The values $d = 2.98$ A.U. and $\theta = 75^{\circ}$, when substituted in equation 8, yield the condition for maxima that $0.222P = n^2 - 0.238\phi$. The values of P for each maximum on curve AB of figure 11 were plotted against various values of n^2 , and the series of points which fell on a straight line parallel to the line $n^2 = 0.222P$ belonged to the correctly ordered maxima.

The difference between the experimental value of the voltage for a maximum and the value given by $P = n^2/0.222$ is the inner potential for that maximum. The average value of the inner potential for the best defined maxima (maxima with $n = 9/2, 5, 11/2, 13/2$, and 7) was 16.9 volts.

An experiment (curve *CD*) without any cooling agent in the grease traps completely changed the shape of the curve, and very weak maxima, if any, could be found. An experiment twenty-four hours later with liquid nitrogen in the grease traps yielded a still different curve without well-defined peaks. The collector current was greater, owing, more than likely, to the better vacuum conditions. It seems reasonable to suppose that during the second experiment the organic vapors present were decomposed by the electron beam at the surface of the galena, thus forming a semi-amorphous layer which remained on the surface for at least twenty-four hours. Consequently, liquid nitrogen on the grease traps failed to bring out any maxima. A dark brown spot was easily seen on the surface of the galena where the electron beam had struck it; this was probably decomposed organic matter. The "fatigue effect" in the case of the oleic acid might be explained on the basis that the electron beam tended to decompose the oleic acid where it struck the surface of the oleic acid and the decomposition product diffused away slowly.

Stearic acid

A minute amount of stearic acid was placed upon a polished platinum plate, the temperature of which was just above the melting point of stearic acid. A thin visible film of stearic acid formed over the surface of the platinum and was quite homogeneous when cold. No maxima and minima were found, and the visible film of stearic acid disappeared. In all probability the film had evaporated in the high vacuum, and something less than a monomolecular film was left.

SUMMARY

Slow speed electrons were used to study various surfaces by means of electron diffraction. The angle of incidence was kept fixed and equal to the angle of reflection, while the accelerating voltage of the incident electron beam was varied. The collector current-accelerating voltage curve showed three broad distinct maxima with a surface of bulk liquid oleic acid, which corresponded to a distance of 3.2 A.U. A long distance of 45 A.U. was also found for oleic acid when the incident beam made a small angle with the surface of the liquid. Oleic acid showed a pronounced "fatigue effect," probably due to a growing surface charge. The (100) cleavage plane of sodium chloride gave maxima corresponding to an inner potential of zero and one of approximately 10 volts. Two methods of measuring were found which apparently did not show a fatigue effect.

The (100) cleavage plane of galena gave no well-defined maxima at room temperature. At 206°C. several well-defined maxima were found which corresponded to an inner potential of about 16.9 volts. Half-order, as well as whole-order peaks were found. Bombardment of the surface with slow speed electrons, at 206°C. and in the presence of a trace of organic vapor, permanently destroyed the grating properties of the galena surface. Stearic acid films on a polished platinum surface vaporized in the high vacuum before an experiment could be performed.

REFERENCES

- (1) BUHL, A., AND RUPP, E.: *Z. Physik* **67**, 572 (1931).
- (2) DAVISSON, C. J., AND GERMER, L. H.: *Phys. Rev.* **30**, 705 (1927).
- (3) MAXWELL, I. R.: *Phys. Rev.* **44**, 73-6 (1933).
- (4) RÄTHER, H.: *Z. Physik* **78**, 527 (1932).
- (5) SOGANI, C. M.: *Indian J. Physics* **2**, 97 (1928).
- (6) THOMSON, G. P.: *Proc. Roy. Soc. London* **1**, 133 (1931).

POLYMOLECULAR FILMS: MIXED FILMS WITH TWO OR MORE COMPONENTS. I

FATTY ACIDS AND NON-POLAR SUBSTANCES¹

ROBERT J. MYERS AND WILLIAM D. HARKINS

Department of Chemistry, University of Chicago, Chicago, Illinois

Received June 11, 1936

I. INTRODUCTION

Monomolecular films of insoluble substances containing a polar group have been extensively examined by Harkins, Langmuir, Adam, Rideal, and other workers. Very little attention, however, has been paid to the more general case of polymolecular films composed of two or more substances. In 1925 Harkins and Morgan (6) examined the force-area characteristics of mixed films of stearic acid and phenanthrene, and showed that the stearic acid exists as a monomolecular film while the molecules of phenanthrene are mostly piled up over it, and the two together give a polymolecular film. de Haas (3) has recently examined films of mixtures of palmitic acid and paraffin, but the films exhibited quite anomalous characteristics.

In view of the great value of a knowledge of the behavior of polymolecular films as a fundamental approach to a generalized theory of surface films, as well as the application of such knowledge to the practical problems of lubrication and cell-interface phenomena, cases in which polymolecular films exist beyond a doubt, the authors have undertaken an extensive investigation of these polymolecular films. Since the films studied both by Harkins and Morgan and by de Haas were solid films, it is quite likely that some of the phenomena exhibited by the films may have been due to this solidity, rather than to orientation effects alone. For this reason, in this investigation, liquid hydrocarbons were added to the polar substances to insure freedom for reorientation, if any, in the film.

This paper is to be considered as a rapid preliminary survey of the general characteristics of films of fatty acids to which were added, before spreading, various quantities of tetradecane or Nujol, non-polar hydrocarbon liquids of relatively low vapor pressure.

II. APPARATUS AND PREPARATION OF FILMS

The film balance, of the type designed by Adam (1) and modified by Harkins and Freud (2) and Harkins and Fischer (4), has recently been

¹ Presented at the Thirteenth Colloid Symposium, held at St. Louis, Missouri, June 11-13, 1936.

further modified and is described in detail elsewhere (7). The torsion head is shown in figure 1, and the film balance in figure 2. The recent improvements may be briefly summarized as follows: (1) A beam arrest, operating much as the balance beam arrest on an analytical balance, is mounted on the torsion head as shown and serves to prevent large movements of the torsion wire-float assembly during a calibration or a determination of film pressure. This has resulted in precise calibrations and exact checks of "zero-point" readings. (2) The trough, 75 cm. long and 25.4 cm. wide, is supported by adjustable screws which in turn are mounted on amber posts for insulation purposes. The plate-glass sides of the box are covered with fine copper screens which are grounded, together with the chromium-plated framework. (3) The box containing the film balance

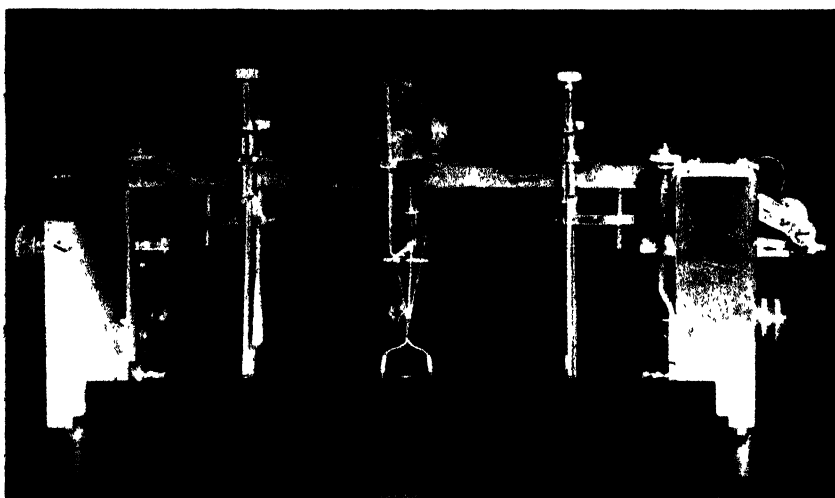


FIG. 1. The torsion head

is enclosed in a larger thermostatically controlled chamber, which may also be closed and grounded, enabling the experiments to be conducted under any desired gas and in total darkness, if necessary. (The work reported here was conducted at room temperature, prior to the construction of the thermoregulating devices.) (4) The surface is swept and the film compressed by means of barriers operated by rods extending to the outside of the box. The threaded lead-screw driving the compression barrier-holder is fitted on the exterior with a mechanical revolution counter, and areas are read in terms of revolutions of the lead-screw. Higher precision in area determinations is thus obtained. (5) The electrodes for contact-potential measurement are carried along the axis of the trough by a moving table which also serves as part of the top of the

inner box. This moving top slides in grooved bars across the top of the box and is also moved by a lead-screw. (Potential measurements reported in this paper were made on the apparatus of Harkins and Fischer, as the potential circuit was under construction at the time of the experiments.) This arrangement of the movable electrodes minimizes the number of moving parts over the trough, and in turn avoids to a great extent the danger of dirt falling upon the surface. (6) The divided drum attached to the torsion wire was mounted on the outside of the box, enabling all readings to be made on the exterior of the apparatus.

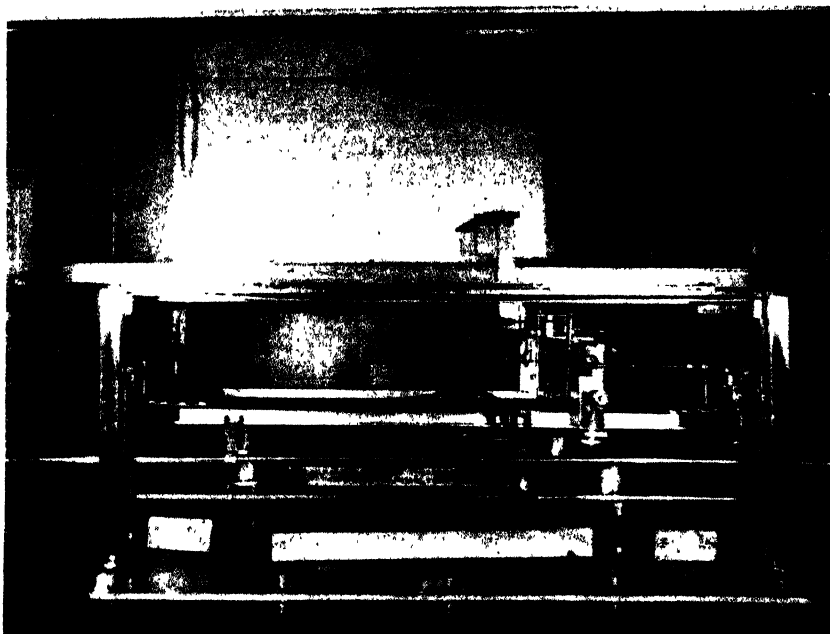


FIG. 2. The film balance

The fatty acids and the hydrocarbons were spread from ligroin as solvent. The ligroin was treated with activated silica gel followed by a distillation in an all-glass apparatus. The hydrocarbons, tetradecane and Nujol, were treated with fuller's earth and then centrifuged. Blank tests made on these purified materials failed to show any traces of spreading substances. The saturated fatty acids were generously loaned for this work by Professor E. Emmet Reid of the Johns Hopkins University. They were prepared by Miss Jane Dick Meyer and are of the very highest purity. The oleic acid was prepared by Dr. Robert J. Moon in this laboratory, by evaporation in a high vacuum. It was exceptionally pure and free from saturated acids.

The solutions for spreading were made by dissolving from 30 to 50 mg. of fatty acid in about 32 g. of ligroin. A special weight pipet designed by Harkins and Freud was used in dropping the material on the surface. The capillary tip was ground flat according to the directions of Harkins and Humphery (5) for the preparation of drop-weight tips. The drops formed slowly and broke off neatly, leaving a negligible quantity on the tip face. In this manner the evaporation error was entirely eliminated. A balance weighing to five decimals was used, since an error of 0.2 mg. in preparing the solutions or in weighing the pipet may result in as much as 1 per cent error. Assuming that all the errors are additive, we feel that the results reported herein are reproducible to less than 1 per cent.

In some cases the shift in the F - A curve produced by the added hydrocarbon is quite small. To eliminate the slight shift between curves caused by a weighing error between two solutions, the hydrocarbon was added directly to a weighed portion of the fatty acid solution, instead of attempting to prepare a new solution of the fatty acid.

III. FORCE-AREA RELATIONSHIPS OF FILMS OF FATTY ACIDS MIXED WITH TETRADECANE

The force-area curves of films of myristic, pentadecylic, stearic, and oleic acids mixed with various quantities of tetradecane or Nujol are shown in figures 3 to 9. All films were examined on 0.01 molar hydrochloric acid.

The lack of any appreciable effect of tetradecane on the force-area curves is quite striking. The effect of longer time intervals between points is shown in experiments 88 and 89 (figure 3). If readings are taken 2 minutes after a film is adjusted to a certain increment of pressure, during which time the areas are decreased sufficiently to maintain the film pressure constant, the curve of experiment 88 (figure 3) is obtained. If the film is held at each pressure level for 4 minutes, the curve of experiment 89 (figure 3) is obtained. These and other experiments point definitely to a need for the development of a standard rate of compression. This problem will be studied during the course of these investigations. For this preliminary survey an arbitrary interval of 4 minutes was adopted, except in those instances in which the "4-minute curve" was unchanged from the "2-minute curve."

The curves of figures 4 and 5 further illustrate the lack of effect of tetradecane on the force-area curves of myristic and pentadecylic acids. At this point in the work it was felt that an evaporation of the tetradecane was taking place. To prevent some of this evaporation, small quantities of dotriacontane² were added to the fatty acid-tetradecane mixtures

² The dotriacontane was generously supplied by Dr. B. J. Mair of the National Bureau of Standards, U. S. Department of Commerce, Washington, D. C.

without appreciable effect. In the case of myristic acid (experiment 100, figure 5) the addition of dotriacontane displaced the F - A curve to larger areas, but the curve was parallel to that without dotriacontane. Examination of the film showed that it was solid, hence it was feared that some

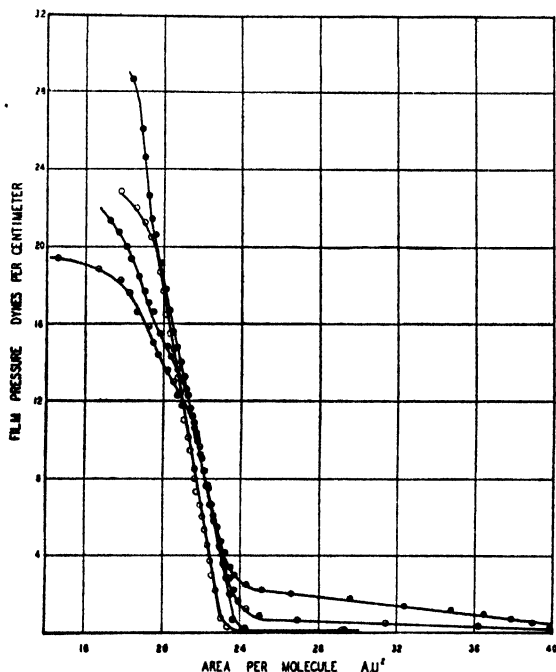


FIG. 3. Stearic acid-tetradecane mixtures

	EXPERIMENT NO	MOLE RATIO		TEMPERATURE IN °C.	ΔT IN MINUTES
		Stearic acid	Tetradecane		
○	91	1	0	22.0	2
●	85	1	10	20.6	2
◐	88	1	50.5	22.0	2
◑	89	1	50.5	22.0	4

Areas per molecule have been calculated on the assumption that all the fatty acid is at the water surface. The experimental points are shown for a single experiment, although check determinations verify the position of the curve drawn. The concentrations with tetradecane are given in mole ratios; those with Nujol in composition by weight, for lack of data on the molecular weight of Nujol.

mechanical resistance due to the solidity might have produced the shift to larger areas. To restore the film to a liquid condition the tetradecane content of the solution was increased, when the curve of experiment 101 (figure 5) was obtained. The large amount of tetradecane has the effect

of increasing the areas greatly at low pressures, but as the film is compressed, the curve approaches that of myristic acid and collapses at nearly the same pressure. It is worthy of note that upon slow compressions of this character (time intervals 4 minutes) the myristic acid films collapsed at pressures but slightly above the kink point in the curve. This is quite different from the second curved portion above the kink in the F - A curve

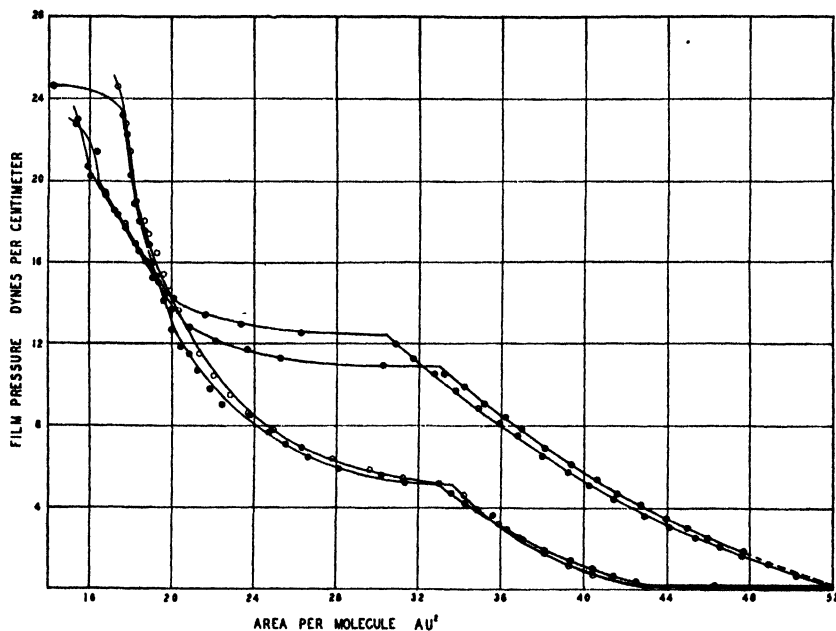


FIG. 4. Mixed films containing pentadecylic acid

	EXPERIMENT NO.	COMPOSITION	TEMPERATURE IN °C.	ΔT IN MINUTES
○	116	Pentadecylic acid	22.1	4
●	97	1 mole pentadecylic acid and 16 moles tetradecane	22.8	4
◐	117	0.77 g. pentadecylic acid and 1.0 g. Nujol	22.1	4
◑	111	0.68 g. pentadecylic acid and 1.00 g. Nujol	24.4	4

obtained by Adam (1). The pressures at the kink point are approximately the same as those given by Adam, but the areas throughout are somewhat smaller. We have attributed this to the high purity of our materials, inasmuch as a small amount of short-chain impurity would influence the areas more than the collapse pressures.

In view of these results with tetradecane and dotriacontane it was felt

that a more non-volatile liquid hydrocarbon would be preferable, as the error due to evaporation would be thereby lessened. The commercial hydrocarbon Nujol (Standard Oil Company of New Jersey) was selected for its purity, non-volatility, and low cost. In working with Nujol, it was possible to place large pans of the hydrocarbon below the film balance, in the interior of the box, through which a stream of nitrogen gas bubbled slowly, to saturate the air with Nujol vapor.

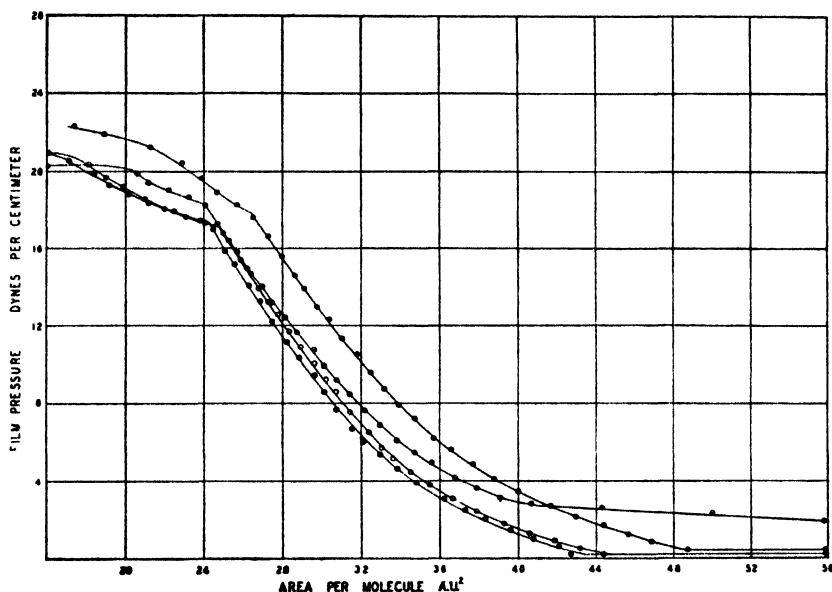


Fig. 5. Mixed films containing myristic acid

	EXPERIMENT NO.	COMPOSITION—MOLE RATIO			TEMPERATURE IN °C.	ΔT IN MINUTES
		Myristic acid	Tetradecane	Dotriacontane		
○	98	1	0	0	22.3	4
●	99	1	12.46	0	22.4	4
◐	100	1	12.46	1.10	22.6	4
◑	101	1	76.21	1.10	22.6	4

IV. FORCE-AREA RELATIONSHIPS OF FILMS OF FATTY ACIDS MIXED WITH NUJOL

Quite contrary to the case of tetradecane, the addition of Nujol to fatty acids produced great changes in the force-area curves of *expanded* films. In the case of stearic acid, a liquid condensed film, the addition of Nujol changed slightly the slope of the compression curve of stearic acid and facilitated collapse at a lower pressure (experiment 110, figure 6), but the areas at zero compression were the same as stearic acid alone, within

experimental error. It is quite possible that larger amounts of Nujol would effect a change in the F - A curve, and this will be investigated.

In the case of myristic, pentadecylic, and oleic acids, the addition of Nujol produced marked effects on the F - A curve. Upon the addition of 1.67 g. of Nujol to 1.0 g. of myristic acid (experiment 106, figure 7), the character of the F - A curve is changed, giving larger areas at lower pres-

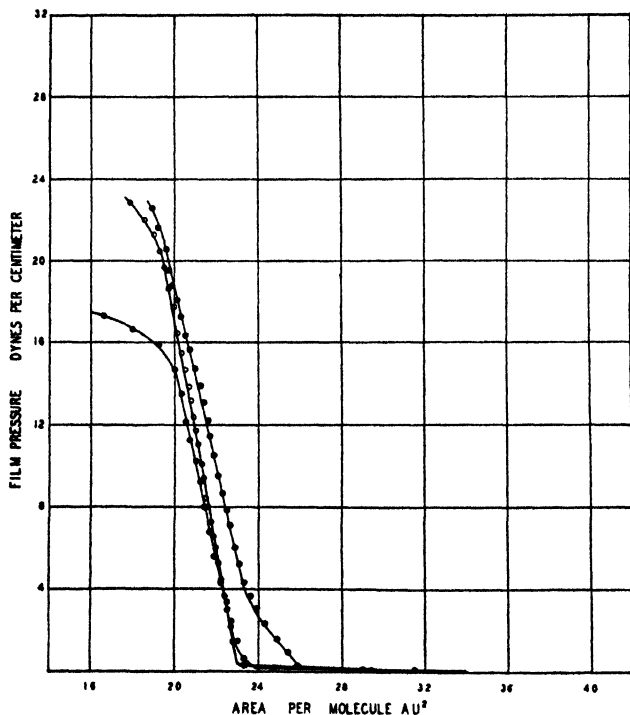


Fig. 6. Mixed films containing stearic acid

	EXPERIMENT NO.	COMPOSITION	TEMPERATURE IN °C.	ΔT IN MINUTES
○	91	Stearic acid	22.0	2
●	93	1 mole stearic acid, 0.95 mole dotriacontane, and 0.95 mole tetradecane	21.7	2
◐	110	1 g. stearic acid and 1.61 g. Nujol	23.5	4

ures, the curve approaching that of myristic acid alone at high pressures. No kink appears in the curve, and the area at zero compression is nearly 10 A. U.² larger. The collapse point is the same as for myristic acid alone.

Upon the addition of Nujol to give 9.08 g. of Nujol per gram of myristic acid, the curve cuts across the myristic acid curve at 13 dynes, exhibits no

kink, and continues without appreciable change in slope down to very small areas. The area at zero compression is again some 10 A.U.² larger. With a concentration of 49.8 g. of Nujol per gram of myristic acid, and in addition 31.5 g. of tetradecane, the film exhibits even less adhesion to the water surface. The area at zero compression is some 8 A.U.² more than that of myristic acid alone. No kink point in the curve was observed, and upon compression to very small areas small lenses were visible to the eye.

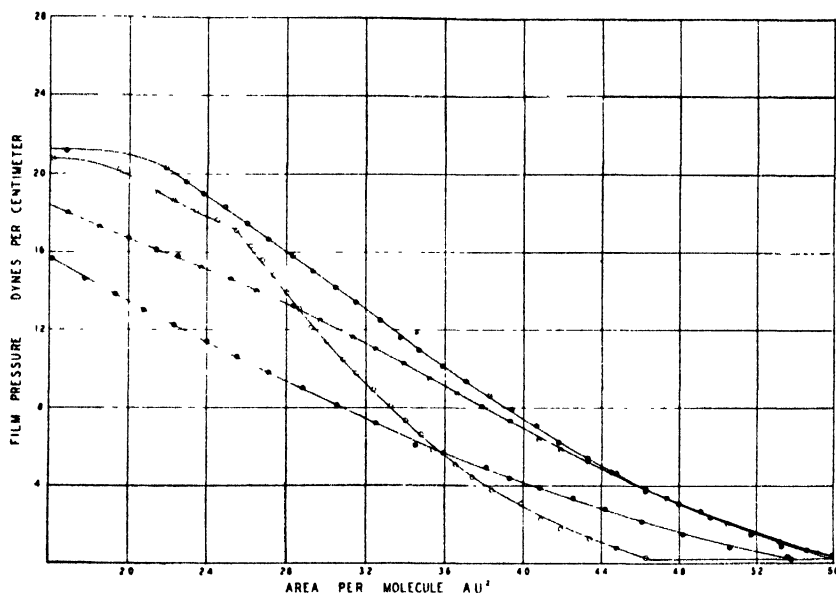


FIG. 7. Mixed films containing myristic acid and Nujol

	EXPERIMENT NO.	COMPOSITION IN GRAMS			TEMPERATURE IN °C.	ΔT IN MINUTES
		Myristic acid	Tetradecane	Nujol		
○	102	1	0	0	22.8	4
●	104	1	31.5	49.8	21.8	4
◐	105	1	0	9.08	22.4	4
◑	106	1	0	1.67	22.9	4

This was the only film on which lenses visible to the eye were noticed. It is quite possible that microscopic lenses may be present; the films are being reexamined by optical methods to determine if the upper surface is heterogeneous. It is to be understood that these films exhibit slight contractions all along the curve, and that the "4-minute" points do not necessarily represent equilibrium areas at that particular pressure. Other time intervals may very well give rise to other curves, indicating again the

great need for extended work on the character of a force-area curve as influenced by the rate of compression.

Experiments 111 and 117 (figure 4) illustrate a most interesting effect of the addition of Nujol to pentadecylic acid. The curves are very similar in shape to that given by pentadecylic acid alone; in fact, are quite parallel throughout the expanded range. The area at zero compression is some 9 A.U.² larger when 1.0 g. of Nujol per 0.77 g. of pentadecylic acid is pres-

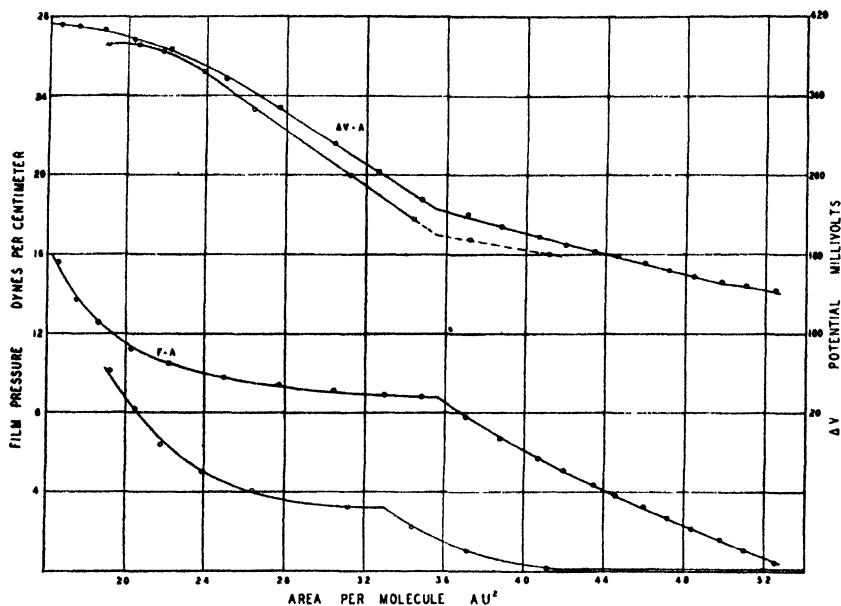


FIG. 8. Pentadecylic acid films

	EXPERIMENT NO.	COMPOSITION	TEMPERATURE IN °C.	ΔT IN MINUTES
○	121	Pentadecylic acid	20.5	4
●	120	0.77 g. pentadecylic acid and 1.00 g. Nujol	20.5	4

ent. The kink occurs at nearly the same area, but some 6 dynes higher, at the same temperature. Beyond the kink a most interesting very flat portion appears which extends to a region around 21 A.U.², where the curve meets that of pentadecylic acid and again rises, but with less slope. The presence of the Nujol appears to facilitate collapse at a lower pressure. The flat portion of the curve suggested some sort of phase transition, and an examination of the contact potentials (4) of pentadecylic acid films with and without Nujol was undertaken to determine if any change

occurred in the ΔV - A curves at this point. The results were most interesting, although they are to be considered as a very preliminary investigation of the contact potentials of the films (figure 8). The ΔV - A curve of the mixed film consists mainly of two straight lines which intersect at exactly the same area as the kink in the F - A curve. A very cursory examination of a pentadecylic acid film at the same temperature showed a similar break in the ΔV - A curve at the same point, although the kink

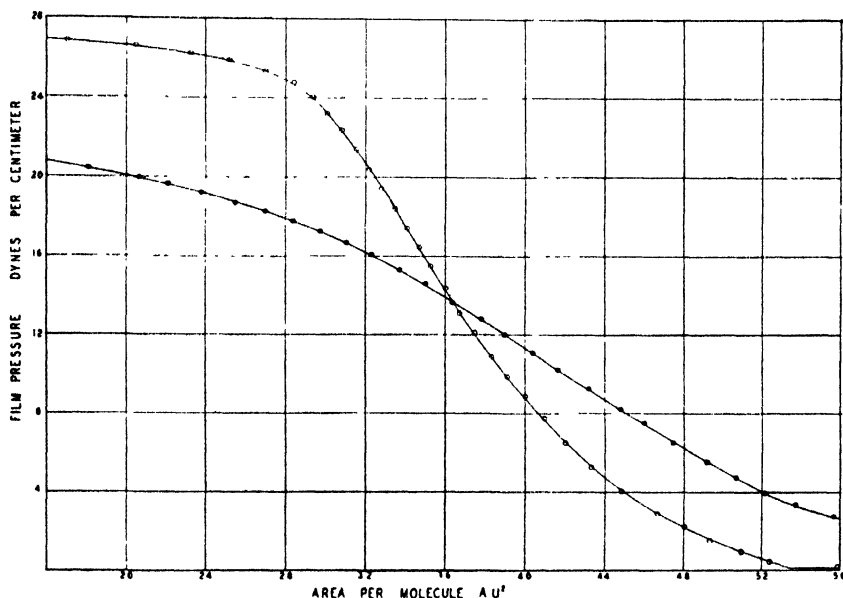


FIG. 9. Oleic acid films

	EXPERIMENT NO.	COMPOSITION	TEMPERATURE IN °C.	ΔT IN MINUTES
○	107	Oleic acid	25.4	4
●	119	0.54 g. oleic acid and 1.00 g. Nujol	24.1	4

in the F - A curve came at an area some 2 A.U.² smaller. In view of the lack of sufficient data at this time, it appears hardly worth while to speculate on the nature of this interesting relationship.

In the case of oleic acid (figure 9) the addition of Nujol caused a marked change in the film. The F - A curve crossed that of oleic acid at about 14 dynes, and extrapolated to an area at zero compression of about 70 A.U.² as compared to 54 A.U.² for the acid alone. Collapse set in much sooner when Nujol was present.

V. GENERAL DISCUSSION

The work reported here was done as a preliminary survey of the field. For this reason it is not possible to formulate any exact explanation of the effects observed. A few points, however, seem quite definite at this time. The marked difference between the effect of the addition of Nujol and that of tetradecane seems to indicate that almost all of the tetradecane evaporates from the surface, thus making it unsuited for an investigation of this character. The addition of solid hydrocarbons, such as dotriacontane or paraffin, on the other hand, may lead to anomalous results, hence it is advisable to select liquid hydrocarbons of a high degree of non-volatility.

The Nujol appears to affect most markedly the expanded portion of the F - A curve. It is reasonable to suppose that in this region some of the hydrocarbon gets down to the water surface, increasing the area per molecule of fatty acid. As pressure is applied, the hydrocarbon is probably squeezed up to the top of the film, where it may or may not exert a further influence upon the film, depending upon the quantity of hydrocarbon present. If sufficient hydrocarbon is present, a second phase may be formed, which the fatty acid molecules may enter with ease, and the collapse point of the film is correspondingly lower. If but a small amount of hydrocarbon is present, it is quite reasonable to suppose that it will have but a slight influence on the collapse pressure. This analysis raises the question: When is the mixed film no longer to be considered as a film but as a second phase with polar material at the oil-water interface? Only further work can give a suitable answer to this question.

The lack of any effect of Nujol upon the lower region of the stearic acid curve is quite striking. It may be tentatively ascribed to the rather low concentration of Nujol present.

The absence of lenses visible to the eye on all but one of the films seems to indicate at least a temporary stability of a thick film of a hydrocarbon oil with polar material at the oil-water interface. Thick films of polar material alone have been shown to be very unstable, if sufficient area is present for a monomolecular film to be formed. There is, however, the distinct possibility that thick films such as those studied here may be quite stable. In any case, it seems evident that a further study of these polymolecular films promises results of the greatest interest, both theoretically and from the practical viewpoint.

The presence of the hydrocarbon may facilitate phase changes in the film, merely by its action as a diluent. The results obtained with pentadecylic acid seem to indicate such an effect. It is more than likely that many obscure points regarding orientation in a monomolecular film may be clarified by aiding reorientation with the addition of a diluent.

VI. SUMMARY

A preliminary survey of films composed of fatty acids and tetradecane or Nujol has been made. The films containing Nujol exhibit many interesting characteristics, justifying further examination of films with two or more components.

REFERENCES

- (1) ADAM, N. K.: *The Physics and Chemistry of Surfaces*. The Clarendon Press, Oxford (1930).
- (2) FREUD, B. B.: *Dissertation*, University of Chicago, 1927.
- (3) DE HAAS, J. J.: *Chem. Weekblad* **30**, 347 (1933).
- (4) HARKINS, W. D., AND FISCHER, E. K.: *J. Chem. Physics* **1**, 852 (1933).
- (5) HARKINS, W. D., AND HUMPHERY, E. C.: *J. Am. Chem. Soc.* **38**, 228 (1916).
- (6) HARKINS, W. D., AND MORGAN, J. W.: *Proc. Natl. Acad. Sci.* **11**, 631 (1925).
- (7) HARKINS, W. D., AND MYERS, ROBERT J.: *J. Chem. Physics*, November, 1936.

THE APPLICATION OF THE HIGH-SPEED MOTION PICTURE CAMERA TO RESEARCH ON THE SURFACE TENSION OF LIQUIDS¹

E. A. HAUSER, H. E. EDGERTON, B. M. HOLT, AND J. T. COX, JR.

Departments of Chemical and Electrical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts

Received June 11, 1936

The high-speed motion picture camera with a stroboscopic source of light, as developed in the past years at the Massachusetts Institute of Technology (H. E. E.), has permitted the demonstration of many phenomena which so far have escaped direct observation. To test the opinion expressed by one of us (E. A. H.) that this technique might materially assist in obtaining a better insight into the actual mechanism of various physicochemical or colloid-chemical problems, two methods commonly used for the determination of surface tension of liquids—the so-called drop-weight and ring methods—were selected in a first attempt to apply the high-speed motion picture camera technique to such studies.

The large number of methods available for the measurement of surface tension, divisible into static and dynamic ones, is a consequence of the fact pointed out by Freundlich (8), that surface tension essentially determines the shape of the liquid in rest or in motion. The static methods are the following: (1) the direct measurement of curvature of the liquid surface; (2) the method of flat drops and bubbles on surfaces; (3) the capillary-rise method; (4) the method of adhesion plates and rings; (5) the determination of drop weights or volume and gas-bubble pressure. The dynamic methods are as follows: (1) the method of oscillating jets; (2) the method of vibrating drops; (3) the measurement of ripple waves. Many other methods of minor importance have been proposed.

Worthington (27) in 1881 was one of the first workers to utilize the first-mentioned static method. He projected the form of hanging drops of water upon a screen. By suitable measurements of the radii of curvature and the volume of the drop he was able to calculate the surface tension, for which he obtained a value of 73 dynes per centimeter. Later in 1912 Ferguson (6) amplified this work by photographing the drop. He obtained a value of 73.4 dynes per centimeter at 11°C. The most complete work on the forms assumed by drops of liquids hanging from a plane surface

¹ Presented before the Thirteenth Colloid Symposium, held at St. Louis, Missouri, June 11-13, 1936.

and by drops resting on a plane surface which the liquid does not wet, has been carried out by Bashforth and Adams (2).

The capillary-rise method has the simplest mathematical derivation and therefore probably has given the most accurate results. The theory in its simplest form assumes only that the liquid wets the tube perfectly, i.e., has a contact angle of zero, an assumption which seems to be justified for water and most of the common organic liquids against glass. The experimental difficulties, however, are large, for it is by no means easy to obtain truly uniform tubes, and to keep them absolutely clean. It is furthermore difficult to measure the height accurately. The method, therefore, is not suitable for rapid or routine work. Modifications of this method have been used by Ferguson (7), Kiplinger (14), and Jaeger (13).

The method of adhesion plates and rings has been used with many variations. The force necessary to draw a horizontal plate, a vertical plate, or a horizontal bar from a liquid surface furnishes the basis for several methods. The two most commonly used instruments are the du Noüy tensiometer (5) and the torsion balance developed by Lenard, Dallwitz-Wegener, and Zachminn (16).

A rough approximation for the surface tension by the du Noüy method can be made as follows: the force necessary to break the ring away from the surface is equal to the surface tension of the liquid multiplied by twice the length of the loop, since two films of water are broken away, one on each side of the ring, or, in another form,

$$\gamma = \frac{P}{4\pi r}$$

where P is the breaking force on the ring in dynes and r is the radius of the ring in centimeters. This is at best only an approximation. For this equation to hold, the two surfaces on each side of the wire must be vertical at the point of breaking, the ring must be truly horizontal, and the column of liquid held up directly under the wire must be negligible. The mean radii of the two surfaces would have to be the same as the mean radius of the loop. For large loops, several centimeters in diameter, made from wire of very small cross section, these conditions are approached quite closely. However, for small loops, such as used in the du Noüy instrument, none of these conditions is perfectly realized. The surfaces are probably never perpendicular, and a fair quantity of liquid is actually supported under the wire itself. Dorsey (4) has given an excellent discussion of this method and its faults.

Tichanowsky (26), Cantor (3), and Lenard (17) have developed better equations for this case, but they still may give results several per cent in error. Harkins, Young, and Cheng (11) have attempted a standardization of this method by comparing the values obtained in using rings of different

sizes with numerous liquids whose surface tension was accurately known. Their equation is:

$$\gamma = \frac{P}{4\pi r} F$$

where F is a correction factor, which they discovered depended only on R , the radius of the ring, and r , the radius of the wire itself. They claim an accuracy of ± 1 per cent, and give tables of F for various values of R/r .

The du Noüy tensiometer is very rapid and easy to use, and the results are easily reproducible. It has proved of outstanding value in recording the change of surface tension in a liquid where adsorption is taking place in the surface (solutions of capillary-active substances).

The drop-weight method is also a very common method for the determination of surface tension. It consists in weighing drops falling from the end of a vertical tube. Although the mathematical theory has not been completely worked out, the method has been widely used because of its simplicity and rapidity.

The actual mechanism of fall is very complex, as will be demonstrated. Briefly, the drop grows larger and longer on the end of the dropping tip; then instability sets in, and a large part of the drop breaks off, leaving a narrow stem attached to the remainder of the drop. At the moment when the drop actually breaks off, it is nearly spherical. The narrow neck then breaks off from the main body of the liquid, and spontaneously constricts at one or more points, as revealed by the high-speed motion picture, followed by the formation of one or more droplets. A single secondary drop has been observed by early workers.

Guthrie (9) in 1863 observed the influence on the size of his drop of rate of fall, temperature, composition of the drop, and the sphere from which he caused all his drops to fall. He observed the formation of a secondary drop which "apparently" was projected up from the upper surface of the drop. Tate (25) in 1864 postulated that "other things being equal, the weight of a drop of liquid is proportional to the diameter of the tube from which it is formed," without himself actually going so far as to state that the weight of a drop falling from a tip is equal to the "circumference of the tip \times surface tension," or $w = 2\pi r\gamma$, which today quite commonly is called Tate's law. It assumes that the entire drop falls off from the tip, while actually only about 60 per cent of it does. Worthington (27) also observed a secondary drop, and concluded quite correctly that "the secondary drop is due to the spontaneous segmentation of the cylindrical neck of liquid, which joins the upper and lower portion up to the last moment before complete separation takes place, and that it is the same phenomenon that was first observed by Plateau (22) in his experiments on mercury." Guye and Perrot (10) in a comprehensive experimental treatise studied the

shapes of dynamic drops. It should be noted that part of this work was done with a motion picture camera taking sixteen pictures per second. They, too, observed the formation of a secondary drop. However, they were of the opinion that the second drop forms from the stem immediately when the first drop falls, and also that just prior to the falling off of the main drop there is a visible oscillation of the surface of the drop. Morgan (21) and his coworkers found "that under certain definite conditions the drop weights of liquids dropping from any one tip are proportional to their surface tensions at the same temperature." The mathematical theory involves, as Adam (1) points out, two points: the size of the drop at the point where instability sets in, and the fraction of the drop which falls. The mathematical theory has been incompletely worked out, but Lohnstein's (20) work is the most thorough. He predicted that the fraction which breaks off is a function of r/a , where r is the radius of the tip, and a is the square root of the capillary constant. Harkins (12) found, as Lohnstein predicted, that the weight of the drop which falls is proportional to r/a and also to another dimensionless ratio $r/V^{1/3}$, where V is the volume of the drop which falls. He verified this assumption for three different organic liquids and for water. Harkins and others have pointed out the necessity of using a very accurately formed tip,—one that is truly flat and circular and with truly sharp edges. A common form is the Traube stalagmometer, which was used in this work. According to Traube's method the number of drops of water falling in a given volume is counted, and then for an unknown liquid the number of drops is counted which fall from the same volume. The surface tensions are presumed to be given in this ratio:

$$\frac{\gamma_A}{\gamma_B} = \frac{N_{B\rho_A}}{N_A\rho_B}$$

where N is the number of drops and ρ is the density of the liquid. It is a rough approximation only.

Adam (1) has shown that the assumption that the correction factor depends only on r/a and $r/V^{1/3}$ is equivalent to assuming that the fraction of drops of similar shapes which breaks away is the same for all liquids. Adam further notes that if "the verification of this for four different liquid-air interfaces is thought an insufficient basis for measuring the surface tension of an unknown liquid, it may be possible to make a direct photographic test, whether the fraction breaking away is normal for that liquid. It seems unlikely that any error can arise except in case of liquids of high viscosity."

The method of vibrating jets has been developed by Rayleigh (23) and by Bohr (24). If a liquid is forced through an elliptical or triangular

opening, it will tend to assume a spherical cross section and will thus vibrate about a spherical cross section as its form of equilibrium.

The other method which is of interest in this work is the measurement of oscillating drops. Rayleigh (23) developed by dimensional reasoning an equation for the time of infinitely small vibrations of an elliptical drop about its equilibrium shape, a sphere.

$$\gamma = \frac{3}{8} \pi P t^2$$

where P = weight of a drop in grams, t = oscillations per second, and γ = dynes per centimeter. For observing this phenomenon, Rayleigh used an oscillating spark which cast the shadow of the drops on an opaque screen, and by varying the length of the time between the drop fall and the spark flash, he was able to record the successive shapes of the drops. Neither Rayleigh nor Lenard (18) was able to observe the successive changes in shape of a single drop for the duration of its fall. The successive changes in shape observed by them correspond to a series of drops. They observed the successive shapes of different drops at progressive time intervals. Lenard continued this work, timing the fall of the drops so that a falling drop itself interrupted the current and caused the spark to illuminate the next falling drop. When photographic pictures were taken the shortest interval between two pictures was 0.01 second.

Kutter (15) measured drop oscillations by still another method. He found that the depth to which a drop falls under the surface of another liquid of equal density does not proportionately increase with the height of fall, but exhibits a periodic function of the falling time. The drops which strike the surface with their long axes parallel to the water do not sink to as great a depth as drops which strike the surface with their long axes vertical to the surface. Out of the falling time and the maximum depth reached by any one drop the period of oscillation was calculated. The surface tension was calculated by the Rayleigh formula. His experiments gave an average of 7378 mg. per millimeter at 18°C., which in the conventional units is 72.4 dynes per centimeter. His experiments showed that the oscillation is not uniform but that there is a decided difference between the stages maximum-minimum and minimum-maximum, which proves that the main oscillation is partly blurred by secondary oscillations. Lenard undoubtedly encountered his main difficulties here, since he was able to measure only one oscillation.

The experimental part of this research consisted of taking high-speed motion pictures of the drop-weight and ring methods of surface-tension measurements.

A series of pictures using distilled water at different times of drop formation, pictures of nitrobenzene, benzene, glycerol, and of solutions

containing capillary-active substances, as for example triethanolamine oleate, were taken. Pictures of the ring method were taken using water, glycerol, and water containing small amounts of triethanolamine oleate. The series referring to the drop-weight method was run at a speed of 1200 exposures per second; those referring to the ring method at 600 exposures per second.

The electrical and photographic apparatus that was used in this investigation may be briefly described as follows: Since the exact moment at which a drop will break off is rather uncertain, it was necessary to operate the camera for as long a time interval as possible. This was accomplished by mounting a camera of the continuously-moving-film type on its side in order that a long, narrow picture could be taken. In this manner several exposures (four or five) could be taken on a single 35-mm. frame, thus materially increasing the duration of elapsed time covered by

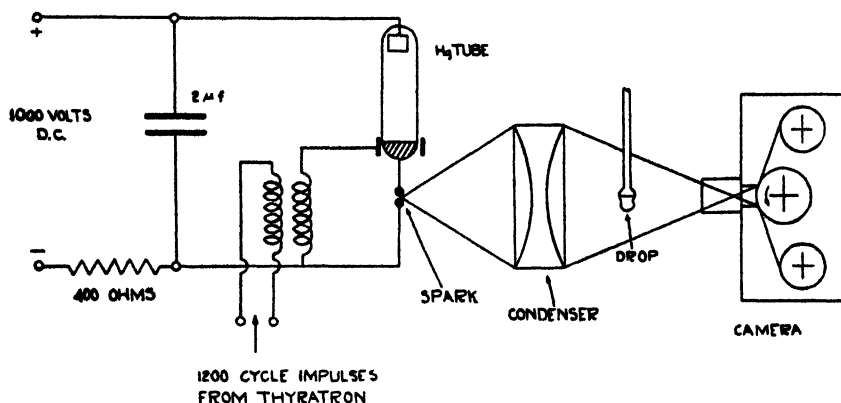


FIG. 1. Schematic diagram of high-speed camera set-up

one film. In order to obtain a satisfactory slow-motion picture of the breaking-off process, the pictures were taken at the rate of 1200 per second, this frequency being secured from a commutator driven by a synchronous motor. The film strips bearing the important exposures were then rephotographed in consecutive order in the normal vertical position on a standard sized 35-mm. film. From this positive prints were transferred and edited on 16-mm. film.

The pictures of the drops are taken by transmitted light as silhouettes which give the outline of the liquid. A spark in air between brass electrodes spaced about one-eighth of an inch apart was used as a point source of stroboscopic light for exposing the photographs. The light was collected by a double-element condenser (10 in. diameter, 10 in. focal length) and directed into the lens of the camera. The object being photographed was located between the condenser and the lens.

Control of the starting of the spark was accomplished by using a pool-type, mercury-arc control tube² in series with the spark gap and the discharge condenser, as shown in figure 1. Between flashes the mercury tube is non-conducting and the 2-microfarad condenser is charged to about 1000 volts from the power supply through the 400-ohm resistor. An impulse of voltage (about 30,000 volts) on the external starting band of the mercury tube causes a spot to be formed on the cathode and allows the 2-microfarad condenser to discharge violently into the spark gap. The mercury tube, besides acting as a switch for turning on the circuit, acts as a rectifier and prevents oscillation of the current through the gap. The impulses of voltage were produced by a thyatron impulse amplifier such as is described in the previously mentioned article.

Special precautions were taken to insure the existence of a saturated atmosphere about the drops, particularly in the cases where the drops were

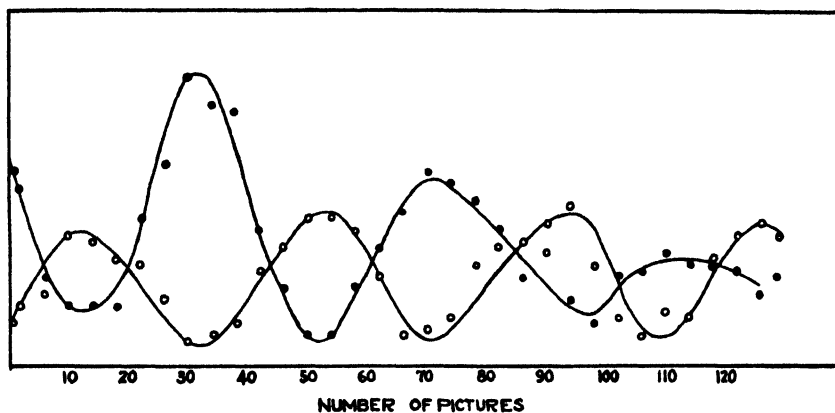


FIG. 2a. Oscillation of benzene drop. 960 pictures per second. Diameter of drop = 0.458 cm. ●, height; ○, width.

suspended for any length of time, in order to avoid evaporation. The apparatus was firmly insulated against vibration. Needless to say, special precautions were taken to have all parts of the instruments scrupulously clean.

The mechanism of the formation of a drop falling off a tip can be described as follows: The drop grows longer and larger on the end of the tip. Instability sets in and a neck forms between the part of the drop remaining on the tip and the part that eventually falls off. This neck grows longer and narrower until the drop finally separates. At this point the drop is slightly ellipsoidal with the long axis vertical. The neck of liquid connecting the two parts of the drop narrows down to a point at the point of

² Such as is described in *Electrical Engineering*, February, 1935, p. 149.

separation (figure 3). The main drop then separates and, owing to the slight tension caused by attachment to the stem, it flattens out somewhat immediately after separation takes place. The main oscillation is marred slightly by secondary oscillations set up at the same time, so that the drop assumes somewhat irregular shapes, though the main effect is a single oscillation about its form of equilibrium, a sphere. A graph showing the variation of the width and length of the drop as it falls is shown in figure 2. The effect of the secondary oscillations can be seen clearly.

The neck of remaining liquid segments at first into a series of nearly equal-sized nodes as shown in figure 4. In all cases observed, the stem of water coalesces rapidly into *one* drop. Sometimes, however, a third drop is projected bodily from the secondary drop with considerable force, in some instances even rising as high as the part of the drop remaining on the

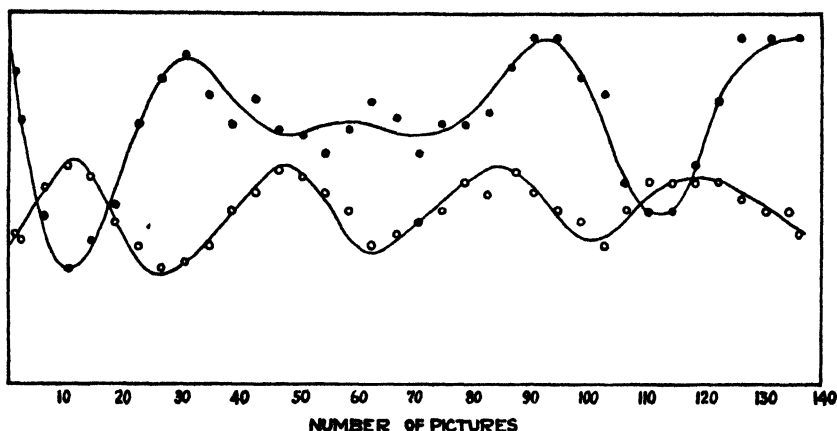
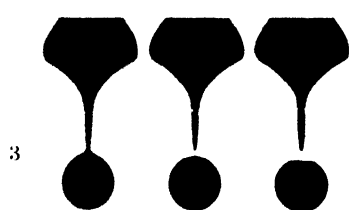


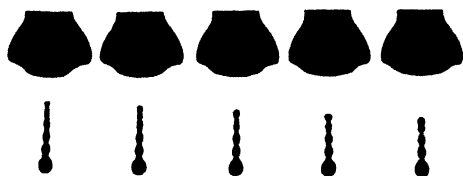
FIG. 2b. Oscillation of water drop, with surface-active substance added. 960 pictures per second. Diameter of drop = 0.476 cm. ●, height; ○, width.

tip, as shown in figure 5. In the case of benzene, owing to the long stem formed, the node formation is exceptionally well pronounced, and the nodes finally break up into one to five drops which follow the main drop (figure 6). The nitrobenzene stem, which is somewhat shorter than the benzene stem, breaks up into three drops (figure 7). These drops fall together a short time after forming and then, contrary to what one might expect, spring apart and continue to fall as three separate drops. This phenomenon might be explained by assuming that electric charges are set up on the surfaces of each droplet which would cause the droplets to be repelled when coming in close contact. Reference should be made here to the work of Lenard (19) on the electric charges of falling drops of water.

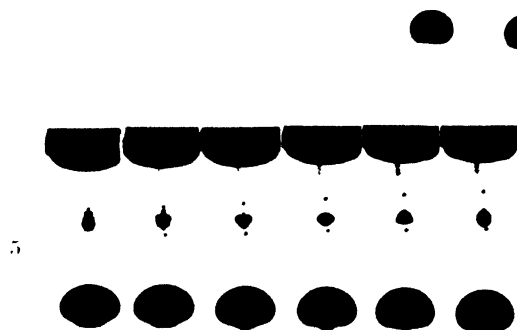
A further suggestion of the presence of electric charges on the surface of the small drops (water) is observed from one of the motion pictures.



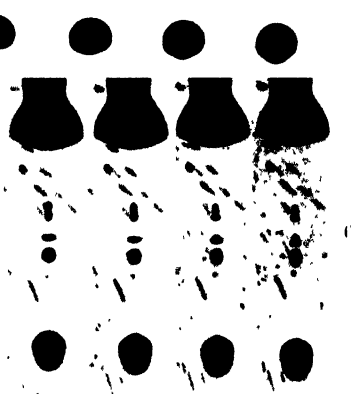
3



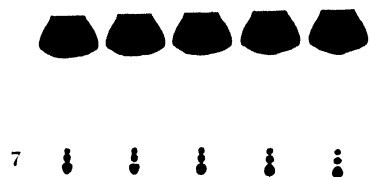
4



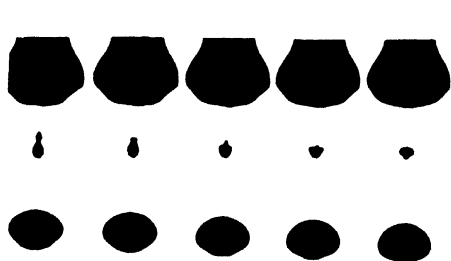
5



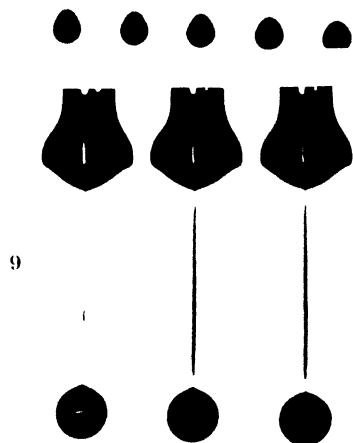
6



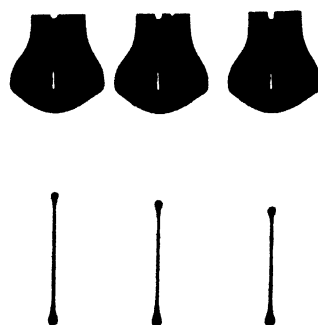
7



8



9



10

FIG. 3. Water
FIG. 5. Water
FIG. 7. Nitrobenzene
FIG. 9. Glycerol

FIG. 4. Nitrobenzene
FIG. 6. Benzene
FIG. 8. Water
FIG. 10. Glycerol

The third drop, which is a very tiny one, is projected upward with such violence that it bumps into the residual drop remaining on the tip and very noticeably bounces back off the surface of the residual drop without joining it. This same effect may be noticed with secondary drops of benzene, for it can very easily be seen from the motion picture that the oscillation of the third and fourth droplets is greatly influenced by the presence of the other drops (figure 6). The third and fourth drops flatten out a great deal more than the others, and while one might expect that the drops would coalesce, they remain definitely apart for their entire period of fall.

In the case of water, the third drop is pinched off from the surface of the second drop at the moment when the column of liquid has coalesced into one drop. One can observe the small drop standing partly out of the surface, having never been quite absorbed by the larger one (figure 5). It is this tiny sphere which is projected upward with violence, probably owing to the surface tension forces operating on the large drop and causing oscillation. The tiny sphere before mentioned is not always projected up from the surface, but quite frequently joins the larger drop permanently (figure 8).

The secondary drop in most cases vibrates very violently and at first somewhat irregularly.

In the case of glycerol, which is a highly viscous liquid, the neck forms as above, but remains attached to the main drop for a much greater length of time, forming at the point of breaking a very fine thread, several times as long as the diameter of the drop (figure 9). Instead of segmenting as the other liquids do, the thread assumes a dumb-bell shape with the drops on each end growing larger and approaching each other very rapidly, until one drop is formed (figure 10). The drop at the lower end falls very slowly in comparison to the rate at which the one at the upper end approaches the lower one, owing to surface-tension forces acting with gravity on the upper end of the dumb-bell being formed and opposing gravity on the lower end.

From the results of drop calculations and measurements, the drops were arranged in order of the size of the main drop. While the correlation was not absolutely perfect, it can be generally said that the drops in all cases observed decrease in size with increase in the time of drop formation, being largest when the drop is formed fastest.

The stem length is the length of the cylindrical stem connecting the two parts of the original drop at the time when the stem separates from the residual part of the drop. This length is easily measured and correlation is perfect. Benzene, forming rapidly, has the longest stem length. Nitrobenzene comes next, followed by the rapidly falling water with the surface-active substance added. Pure water, which forms rapidly, is still shorter, and following it, the stem length decreases in general with increase in time

of formation. The surface-active solutions show a marked progressive decrease in the stem length.

Of interest here is the fact that while the surface tension of the solutions of water containing capillary-active substances was considerably less than that of pure water, the stem lengths were the shortest observed, whereas in the case of pure liquids of low surface tension the stem lengths increased with decreasing surface tension.

Although considerably more experimental work will have to be done to be in a position to offer a satisfactory explanation for this discrepancy in the discovered correlation of stem lengths to surface tension, the following preliminary explanation might be considered. Whereas in a true liquid the molecular composition of the surface layer is the same as the interior of the liquid, in the case of liquids containing capillary-active substances there is a definite concentration and orientation of the molecules of said substance in the surface. This orientation undoubtedly has some bearing on the elastic properties of the surface layer, making it less elastic and

TABLE 1

LIQUID	TEMPERATURE	VISCOSITY η	SURFACE TENSION γ
	$^{\circ}\text{C.}$	<i>centipoises</i>	<i>dynes per cm.</i>
Water.....	20	1 008	72.75
Glycerol.....	30	881.0	63.0 (20°C.)
Nitrobenzene.....	20	2 013	43.9
Benzene.....	20	0 647	28.88

offering a greater resistance to distortion. Therefore, it may be assumed that the stem breaks off more rapidly than is the case with true liquids, where free movement of the molecules should permit further elongation.

We have calculated the volumes of the secondary drops and expressed them in per cents of the volumes of the large drops. For water, the volumes of the secondary drops average 3.12 per cent of the main-drop volumes. The volume of the secondary drop formed from the dumb-bell-shaped stem of glycerol is 5.92 per cent of the main-drop volume. The volume of the secondary drop of nitrobenzene is about 8.45 per cent of the main-drop volume, and the volume of the secondary drops of benzene averages 12.5 per cent of the main-drop volume.

Here again water containing capillary-active substances shows a discrepancy, since the rapidly forming drop gives a slightly higher volume percentage for the secondary drop than does pure water, the more slowly formed ones a smaller volume. This phenomenon stands in perfect accord, however, with the stem length discussed above.

The results of the four cases so far observed seem to demonstrate that

the per cent drop volume of the secondary droplet of pure liquids increases with decreasing surface tension. It furthermore shows that the viscosity of the liquid under consideration seems to have no influence on this effect (see table 1).

CALCULATIONS OF SURFACE TENSION FROM SECONDARY-DROP OSCILLATIONS

This method permits, for the first time, the measurement of surface-tension values by observing the frequency of oscillation of one *single* drop during its *entire* fall. Furthermore, it permits the measurements of surface tension by observing the oscillation frequency of secondary droplets formed. The frequency of these latter observations is decidedly higher than the one with the primary drop. The results obtained with pure liquids gave satisfactory values.

The method furnishes, furthermore, a new tool for the determination of adsorption effects on very recently formed surfaces, which is of outstanding importance in connection with the study of solutions containing capillary-active substances. These observations seem to show that a considerable time is necessary to obtain equilibrium. At least in the majority of cases some adsorption has taken place on the drop surface immediately after forming—the drop oscillation having been measured less than one-tenth of a second after the surface had been freshly formed—but a considerable time has to elapse before perfect equilibrium is obtained.

The ring method

A series of high-speed motion pictures of the ring method were taken at a speed of 600 exposures per second, using distilled water, water to which a capillary-active substance had been added (triethanolamine oleate), and glycerol. The method as revealed by the motion picture camera can be described as follows.

The ring as it is raised pulls up with it a considerable volume of water. At the point of maximum tension the surface of the liquid on the inside of the ring is slightly concave, with the surface at the edge of the ring rather sharply bending up to the ring. In no case are the sides truly perpendicular, which theoretically would be necessary for the measurement of the true value of the surface tension (figure 11). As the ring is pulled further, the surface of the main body of the liquid starts to become more concave, showing an approximate hyperbolic curve; at the same time the surface between the ring drops down considerably as can be seen by the light reflection in figure 12. As the ring is raised further, a conical film of liquid forms below the ring holding up the remainder of the liquid above the surface. This inverted cone then tends to assume its equilibrium shape, a horizontal film, and in doing so imparts to the remainder of the liquid above the surface of the water a vertical force which causes this column of

water actually to shoot above the level of the ring (figure 13). The force which causes the column of liquid to be forced up above the level of the ring is sufficient to project upwards several small droplets in the case of water- which rise nearly to the height of the bar which raises the ring.

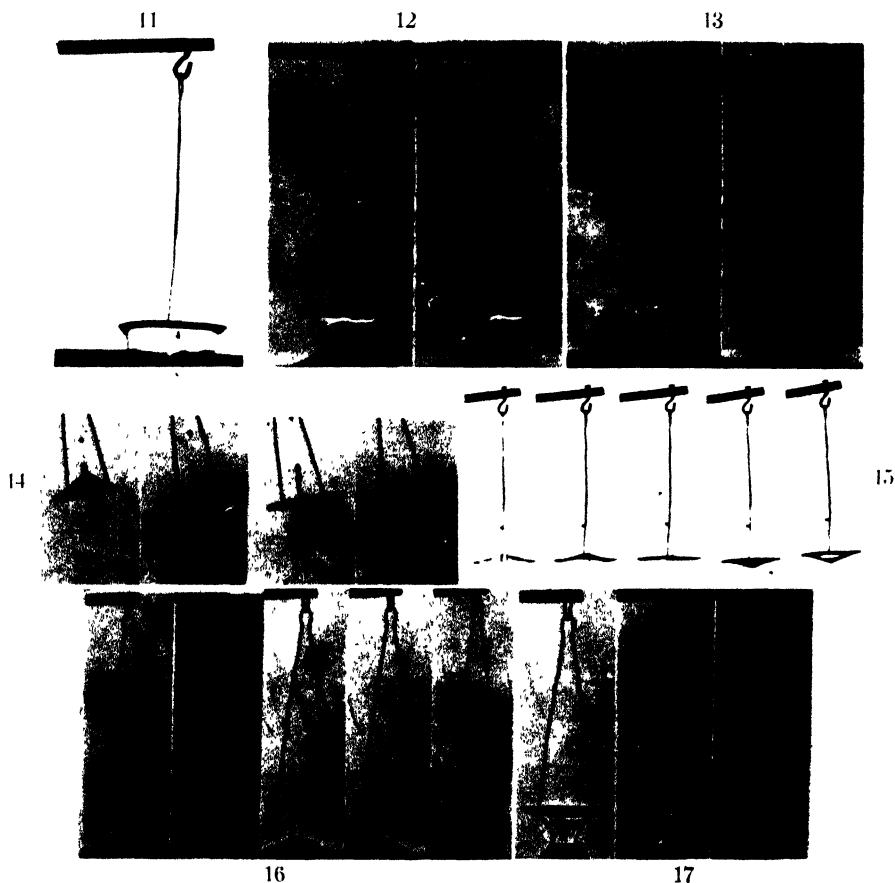


FIG. 11. Tricethanolamine oleate

FIG. 12. Water

FIG. 13. Water

FIG. 14. Water

FIG. 15. Tricethanolamine oleate

FIG. 16. Glycerol

FIG. 17. Glycerol

This column in the case of pure water and of water containing a surface-active substance then falls back and breaks away from the film of liquid left on the ring, finally collapsing into the main body of the liquid. The lamella of water remaining on the ring oscillates rapidly up and down until

the bar to which the ring is attached comes to a stop. Then the film shoots up and forms a short column of liquid, which breaks up into several drops as shown in figure 14. This film oscillation can be better observed in figure 15, which shows water containing 0.01 per cent of triethanolamine oleate. For water 66.3 oscillations per second were observed, while the pictures taken with the above-mentioned solution showed 49 and 50 oscillations per second. The frequency was constant over the entire period which was observed.

If one assumes that the restoring force on the oscillating film is due solely to the magnitude of the surface tension on the film—a good assumption, if the film is very thin and if the viscosity is not great—and also assumes that the mass of the liquid forming the films is the same, then by simple proportion, the surface tension of the film can be calculated. Using the correct value for water of 72.8 dynes per centimeter, the surface tension of the surface-active film would be

$$\gamma = 72.8 \times \frac{50}{66.3} = 54.8$$

which has been ascertained to be the correct value for this liquid. So far as could be ascertained the oscillation of a thin film of liquid has never before been observed, nor used as a method of surface-tension determination.

Glycerol showed another interesting phenomenon. The initial stages of the breaking away were the same as with water, but a thin thread forms very rapidly, connecting the film left on the ring and the surface of the glycerol. As before, the film on the ring imparted a force on the thread of liquid which caused it to shoot up above the level of the ring (picture preceding the first picture on figure 16). The thread sprang back again, but instead of breaking, it again rose very slightly above the level of the ring. At this point it parted in several places along its length and formed several tiny drops which fell back into the main body of the liquid. Owing to the high viscosity there was no film oscillation to be observed on the ring (figure 16).

Another feature of interest is the regular streaks which appear on the conical film of glycerol below the ring before it forms the thread. This seems to show some peculiar orientation of the liquid film under tension.

One would normally not expect that homogeneous liquids would show orientation under any conditions. The orientation of gel structures under tension has long been observed, and the gels are assumed to have a more or less fixed structure which under tension aligns in a definite orientation. These pictures possibly indicate that in the case of viscous liquids there is some alignment which results in the appearance of a streaked surface of

the film under tension. It is hoped that further observations of this sort will throw more light on the structure of liquids (figure 17).

SUMMARY

1. As a first attempt to apply the high-speed motion picture camera to the study of physicochemical or colloid-chemical problems, its application to the study of the mechanism of the drop-weight and ring methods in the measurement of surface tension is described.

2. The successive steps in the formation of drops, as revealed by this technique, are enumerated.

3. The formation of a stem following the main drop has been observed; the segmentation of the stem and the formation of one or more secondary drops is discussed.

4. In a pure non-viscous liquid, it has been shown that the size of the main drop decreases with increase in time of drop formation.

5. For pure non-viscous liquids, the length of the stem increases with decrease in surface tension of the liquid. The influence of viscous liquids on the stem is also referred to.

6. The size of the secondary drop, figured in per cent of the main drop, increases materially with liquids of decreasing surface tension.

7. For water containing capillary-active substances, the length of the stem is shorter than that of the pure water. An explanation for this discrepancy is offered.

8. The measurement of the oscillations of the secondary drops is described as a new means of studying adsorption effects in freshly formed surfaces.

9. The mechanism of the ring method for the determination of surface tension is described and demonstrated.

10. The oscillation of a thin film of liquid is demonstrated, and a possible new method for the determination of surface tension using extremely thin lamellae of liquid is indicated.

11. Interesting observations of the influence of viscosity in the mechanism of the ring method are described.

12. The stroboscopic analysis of the phenomena appearing in connection with surface-tension measurements by the drop-fall and the ring method show motions of such a high degree of complexity as to suggest that neither of these methods is ideal from the standpoint of accurately determining surface tension.

13. To obtain comparable data with solutions of capillary-active substances it seems indispensable to indicate the time of drop formation or rest period of the liquid surface when determining surface tension with the methods discussed.

We wish to express our great indebtedness to Dr. Vannevar Bush, Dean of Engineering, for the interest he has taken in this work and for the facilities he has placed at our disposal.

Our special thanks are due to the Research Associates of the Massachusetts Institute of Technology for a grant-in-aid which enabled us to carry out this project.

REFERENCES

- (1) ADAM, N. K.: *The Physics and Chemistry of Surfaces*. The Clarendon Press, Oxford (1930).
- (2) BASHFORTH AND ADAMS: *An Attempt to Test the Theories of Capillary Action by Comparing the Theoretical and Measured Forms of Drops of Fluids*. Cambridge (1883).
- (3) CANTOR: *Ann. Physik* **47**, 399 (1892).
- (4) DORSEY: *Bull. Natl. Research Council* **69**, 56 (1929).
- (5) DU NOÛY: *J. Gen. Physiol.* **1**, 521-4 (1919).
- (6) FERGUSON, A.: *Phil. Mag.* **23**, 417 (1912).
- (7) FERGUSON, A., AND DOWSON, P. E.: *Trans. Faraday Soc.* **17**, 384-92 (1921-22).
- (8) FREUNDLICH, H.: *Kapillarchemie*, 4th edition, Vol. I, pp. 6-215 (1930).
- (9) GUTHRIE, C.: *Proc. Roy. Soc. London* **8**, 444 (1863).
- (10) GUYE AND PERROT: *Arch. sci. phys. nat.* **15**, 178 (1903).
- (11) HARKINS, YOUNG, AND CHENG: *Science* **64**, 333 (1926).
- (12) HARKINS AND HUMPHERY: *J. Am. Chem. Soc.* **38**, 228-46 (1916).
- (13) JAEGER, F. M.: *Z. anorg. allgem. Chem.* **101**, 1-214 (1917).
- (14) KIPLINGER, C. C.: *J. Am. Chem. Soc.* **42**, 472-6 (1920).
- (15) KUTTER, VICTOR: *Physik. Z.* **17**, 424 (1916).
- (16) LENARD: *Ann. Physik* **74**, 381 (1924).
- (17) LENARD: *Ann. Physik* **74**, 381 (1924).
- (18) LENARD: *Ann. Physik* **30**, 209 (1887).
- (19) LENARD: *Ann. Physik* **46**, 584 (1892).
- (20) LOHNSTEIN: *Ann. Physik* **20**, 237, 606; **21**, 1030 (1906); **22**, 767 (1907).
- (21) MORGAN, J. L. R.: *J. Am. Chem. Soc.* **37**, 1461-7 (1915).
- (22) PLATEAU: *Statique Experimentale et Theorique des Liquides Soumis aux Seules Forces Moleculaires* (1873).
- (23) RAYLEIGH: *Proc. Roy. Soc. London* **29**, 71 (1879).
- (24) RAYLEIGH, BOHR, AND STOCKER: *Z. physik. Chem.* **94**, 149 (1920).
- (25) TATE, T.: *Phil. Mag.* **27**, 176 (1864).
- (26) TICHANOWSKY: *Physik. Z.* **25**, 299 (1924); **26**, 522 (1925).
- (27) WORTHINGTON, A. M.: *Proc. Roy. Soc. London* **32**, 362 (1881).

UNIMOLECULAR FILMS OF NERVE PROTEINS¹

LYMAN FOURS AND FRANCIS O. SCHMITT

Department of Zoology, Washington University, St. Louis, Missouri

Received June 11, 1936

Since the modern developments in the theory of protein structure little work has been done on the characterization of the individual proteins of nerve and on the significance of the colloidal properties of these proteins in determining nerve structure and function. The mere classification of the various nerve proteins is still in considerable doubt and, with the possible exception of the so-called neurokeratin, the localization of these proteins in the nerve axon is altogether unknown. Recent experiments on living axons by means of polarized light have shown that the proteins of the axon sheath are organized in a manner quite different from those in the axis cylinder, and there is some evidence that there may be considerable difference in the molecular architecture of these various proteins. Obviously before the ultimate question of the rôle of these protein structures in nerve function can be answered, these preliminary points must be settled.

The present studies have been designed to aid in the characterization of certain of the nerve protein fractions now recognized. Comparison of the behavior of films of these proteins with films of various other proteins not only yields information of value for an interpretation of nerve structure, but furnishes additional facts for which the general theory of protein films must account.

MATERIALS AND METHODS

The nerve proteins were prepared from the leg and claw nerves of lobsters, according to the method described by Schmitt and Bear (9, 10). The finely cut nerve bits were successively extracted in neutral saline, borate buffer of pH 9 and 11, and in *N*/100 sodium hydroxide. In the fraction previously called neurostromin we now recognize three subdivisions: one coming out in *N*/10 sodium hydroxide and exhausted with successive changes of alkali, another obtained by relatively brief extraction with *N*/2 sodium hydroxide, and likewise diminishing in quantity in repeated extractions, and a third, removed by *N*/2 alkali only after twelve

¹ Presented at the Thirteenth Colloid Symposium, held at St. Louis, Missouri, June 11-13, 1936.

to eighteen hours of reaction. In $N/2$ sodium hydroxide the nerve shreds eventually swell and soften, so that violent shaking suffices to convert previously recognizable shreds into a strongly turbid solution. The main bulk of the nerve vanishes at this stage; strong centrifuging yields only a very small residue quite different from the original nerve fibers. The protein extracted in $N/10$ sodium hydroxide has a flocculation zone beginning at pH 5.5 with a maximum around pH 4.5, as determined turbidimetrically in acetate buffer. The first fraction coming out in $N/2$ sodium hydroxide is also precipitated at pH 4.5 by acetic acid. The fraction obtained after long standing in $N/2$ sodium hydroxide is not precipitated under the same conditions even with prolonged centrifuging. For the present film work only the fractions removed in $N/10$ sodium hydroxide and by brief extraction with $N/2$ sodium hydroxide were used, because of the instability of the fractions obtained with weaker alkalinity. Both preparations were purified by thrice repeated precipitation with acetic acid at pH 4.5. The precipitates were fairly readily redissolved in Sørensen borate buffer of pH 9, yielding stable, slightly opalescent solutions, especially if the precaution of washing out the acetate with a little borate is observed. The final preparation was analyzed for nitrogen by micro-Kjeldahl, the weight of protein being taken as 6.6 times the amount of nitrogen.

The egg albumin used for comparison was recrystallized four times according to the method of Sørensen as described by Morrow (8), and dialyzed in the cold until barium chloride gave no test for sulfate. The protein concentration was determined by drying to constant weight.

Force-area measurements were made with the Adam modification of the Langmuir trough. Surface potentials were measured by a modification of the vibrating condenser method of Yamins and Zisman (11). The film was applied by forcing the solution from a microburet, the capillary tip of which was held just inside the surface. By a rack and pinion stand the tip is pulled up slightly after touching the surface, to minimize the possibility of protein going into the bulk of the subsolution.

GENERAL CONDITIONS OF FILM SPREADING

Three considerations arising from the method of preparation of the nerve proteins may be of significance with regard to their spreading as monomolecular layers. The first is the possibility that nucleic acid from the nuclei abundant in nerve sheaths is dissolved in these extractions. Levene (7) obtained purine bases from the ammonium chloride extract of brain, as well as from a dilute alkali extract. However, Gorter, Ormond, and Meijer (4) have shown that the addition of nucleic acid to protein solutions has no effect, at least upon area per milligram extrapolated to zero pressure.

The second consideration is the unknown partition of the lipids between the different fractions. Although lobster peripheral nerve contains relatively less lipid than does vertebrate medullated nerve, Schmitt, Bear, and Clark (10) obtained x-ray diffraction patterns characteristic of lipids even in nerve protein fibers spun into and extensively extracted with alcohol. Apparently the union is very tenacious; just how the properties characteristic of large arrays of short amino acid residues are modified by hydrocarbon or sterol groups, themselves capable of forming films, remains to be determined.

The third consideration is the possibility of progressive hydrolysis and denaturation of the normal nerve proteins by the strong alkali solutions employed. It must be admitted that the extraction agents bring about permanent changes; for instance, the $N/10$ and first $N/2$ sodium hydroxide fractions after precipitation in acetic acid may be redissolved in weakly alkaline buffer solution of pH 9. However, the fact that at each of these stages the extractions go to completion rather than progressing steadily, seems to indicate that a definite portion of the large structure protein unit is being removed in each case, rather than that an indefinite and generalized attack on all the linkages is occurring.

Of interest in this connection is the fact that upon $N/300$ acetate buffer of pH 4.7 the $N/10$ sodium hydroxide extract forms elastic patches, whereas the $N/2$ extract gives fluid films. This property is observed by the movement of talc particles upon the surface under the influence of gentle puffs of air from a medicine dropper. The validity of interpreting this as indicating a difference in the particle size of the two protein fractions is rendered doubtful by the fact that on dilute hydrochloric acid of pH 2.5 the $N/10$ sodium hydroxide extract forms fluid films which become elastic at a pressure less than 1 dyne per centimeter. A difference in the constitution of the two fractions is more probably responsible for this difference in adhesion.

EXPERIMENTAL RESULTS

After the monomolecular layer of protein has been spread, either by its intrinsic spreading tendency or by the admixture of alcohol (3), it can be further studied by compression to smaller areas. Films not already elastic become so upon compression, and with increasing pressure become quite rigid.

The manner of compression has a marked influence on the type of curve obtained. At each step of compression to smaller areas the pressure rises quickly to a maximum, then decreases to a steady value higher than the previous equilibrium value. The magnitude of this pressure readjustment is shown in figure 1, which presents an experiment in which special care was taken to obtain complete equilibration. The small curves extending

out to the side of each equilibration step having time as abscissae give the course of this adjustment. The irregularities imposed upon the equilibration curves at high pressures are probably due to the rigidity of the film and the difficulty of adjusting the torsion system to an exact balance. This experiment shows several other features: (1) The approximately linear portion of the equilibrium force-area curves which, extrapolated to zero pressure, is used as a quantitative measure of spreading

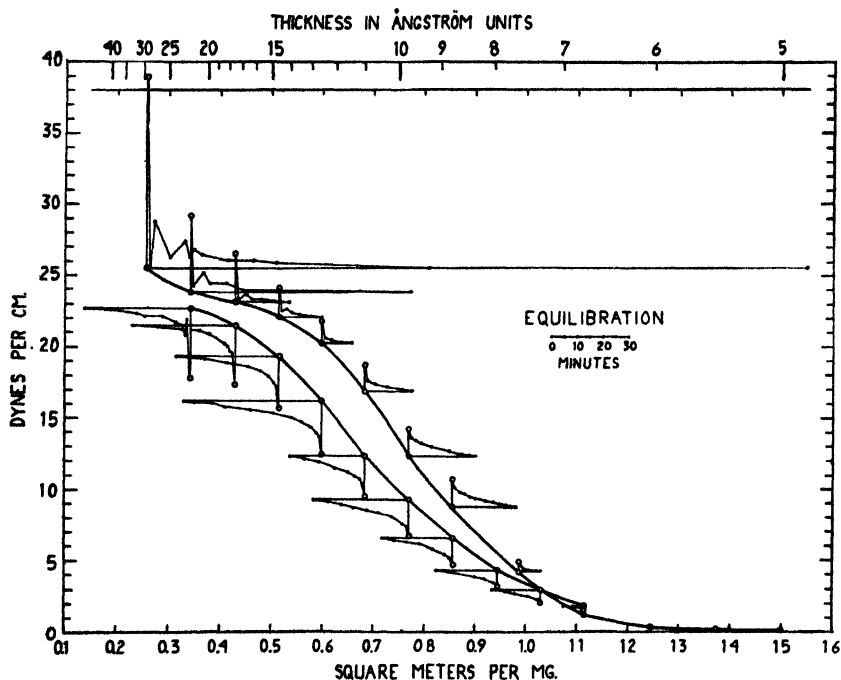


FIG. 1. Egg albumin on $N/300$ acetate buffer, pH 4.6. Unrestricted spreading at 1.5 m.^2 per milligram. Ordinates, surface pressure; abscissae, for open circles, area per milligram of protein; for small points, time after obtaining initial pressure values. The open circles give initial and equilibrium pressure values at each area. The small points show the course in time of the corresponding equilibration. Thickness is calculated from the specific volume (0.75 cc. per gram) for dissolved protein.

area, following the convention of Gorter. (2) At low areas the increase of pressure with decrease in area is less rapid than in the linear portion of the curve. Similar effects have been observed also with casein and myosin. This region we shall refer to as the plateau. (3) Both initial and equilibrium pressure values undergo a final and rapid rise at very small areas. This apparently corresponds to the final close-packed condensed state of molecules with long hydrocarbon chains, such as fatty acids. Other experiments show rapid increases in the equilibrium pressure at lower areas

than those of the plateau. (4) An equilibration takes place in the opposite sense on reexpanding; this must be the reversal of the readjustments made in compressing the film. (5) The compression is reversible throughout the range of areas down to 0.25 m.^2 per milligram, if equilibration is allowed. Further compression brings about a complete buckling of the film, properly comparable to the collapse of a fatty acid film, and irreversible, as noted by Devaux (2). We find, as did he, a tendency for the collapsed film to form fibers. These fibers when transferred to a slide and examined with polarized light showed birefringence positive with respect to the fiber axis. While the stretching necessary in the manipulation may have been

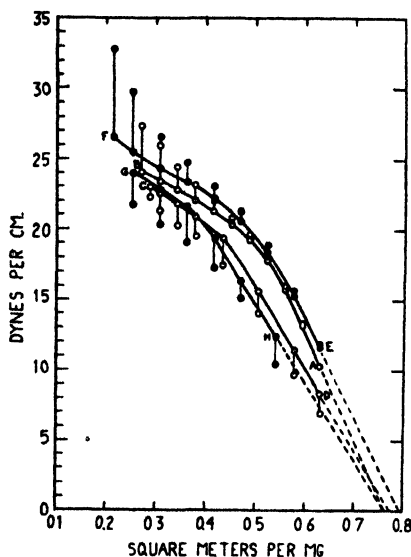


FIG. 2. Egg albumin on $N/300$ acetate buffer, pH 4.6. Restricted spreading at 0.63 m.^2 per milligram. Coordinates as before. Initial and equilibrium pressure values shown at each area. A to B , compression; B to C to D , expansion; D to E , adjust water level; E to F , recompression; F to G to H , reexpansion.

responsible for a portion of the orientation, the fact is interesting as an indication that the protein in the film was in a state of partial degeneration or denaturation and capable, by interaction of side chains, of being integrated into a fibrous structure as postulated by Astbury, Dickinson, and Bailey (1).

The initial points lie on a smooth curve only if the technique of compression, pressure adjustment, and further compression is maintained uniformly, whereas the equilibrium values are independent of further lapses of time, as figure 1 shows. In rapid compression an equilibration debt, as it were, is accumulated, which forces itself upon the attention of

the observer only at relatively high pressures, if compression is rapid and uniform. The amount of equilibration in the first minute after obtaining the initial pressure is small at low pressure as the time curves show in figure 1. As the pressure increases, the fraction of the whole equilibration occurring within the first minute increases very greatly. This should not be confused with the more or less irreversible collapse of the protein film found after the condensed state is reached.

That the compression is reversible above an area of 0.25 m.^2 per milligram is further shown by the experiment presented in figure 2, in which a film of egg albumin is compressed, expanded, recompressed, and reexpanded. Only the initial and equilibrium points are shown at each step.

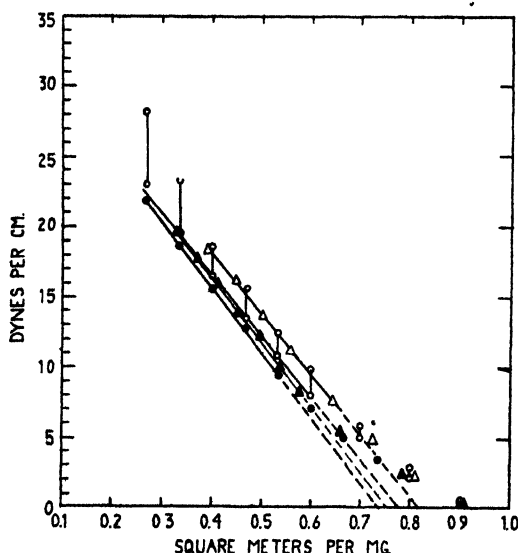


FIG. 3. Nerve protein extracted in $N/10$ sodium hydroxide. Spread on $N/300$ acetate buffer, pH 4.6, with aid of 4.25 per cent alcohol. Coordinates as before. Equilibrium points only, of four separate films, except open circles, which show both initial and equilibrium points.

Comparison of figures 1 and 2 shows that the areas at zero pressure extrapolated from the approximately linear portion of the equilibrium pressure curves are different in the two cases, although the buffer subsolutions were practically the same. This variation has been studied in other experiments and seems to be due to incomplete spreading of the protein when the surface available for its spreading is limited. It is not clear whether this is due to an incomplete uncoiling or degeneration, to use Astbury's term, of the protein from the dissolved (globular) state to its extended condition on the surface, or is caused by a partial passage of protein into the body of the subsolution in the trough. In such restricted spreading the pressure

rises rapidly at first, then gradually approaches an equilibrium value. This spontaneous pressure rise is quite sensitive to the character of the subsolution and to the precise manner of application from the tip of the microburet.

Nerve proteins resemble egg albumin in showing equilibration, but the plateau effect between the linear portion and the final condensed packing is absent. In figure 3 are plotted the equilibrium points of four successive films of nerve protein extracted in $N/10$ sodium hydroxide, spread on $N/300$ acetate of pH 4.6 with the aid of 4.25 per cent alcohol. One set of initial points is included as well to show the similarity to other proteins. However, instead of showing a plateau, the curves at the lowest area seem to be passing over into the condensed packing. This is not so far-reaching a distinction between the proteins as might be thought, however, since casein, which shows the plateau markedly on some subsolutions, shows hardly any upon others. Moreover, definite indications of this plateau have been obtained for nerve proteins of the neurostromin group on other buffers. Fibrinogen films, although showing the plateau upon water, show little or none upon McIlvaine's phosphate-citrate buffer.

The general relations of the phase boundary potentials observed with these films are quite similar to those reported by Hughes and Rideal (6) and by ter Horst (5), using the polonium electrode method. At great areas the potentials fluctuate. With decrease of area, the time average of these potentials tends to rise and the range of fluctuation to decrease, until the potential becomes steady at the area at which the whole available surface is covered with film. In the case of elastic patch films this can be made plainly visible by dusting talc upon the surface previous to spreading. Depending on the resistance of the elastic patches, more or less pressure is required to deform them and thus to fill the available space. The steady potentials increase with decreasing area without showing any equilibration to correspond to the force changes within the sensitivity of our measurements (1 or 2 millivolts). At lower areas the potential levels out, becoming constant and independent both of area and pressure. This constant potential region extends into the final upturn of the force-area curves for condensed packing. Through the region of largest equilibration the potentials remain constant.

In spreading at restricted areas the potential changes cease long before the increase in pressure reaches equilibrium. This has been observed with fibrinogen on phosphate-citrate buffer of pH 7.4. Egg albumin on $N/300$ acetate, pH 4.65, shows a somewhat greater tendency for the potentials and pressure to change together, but even here the potential curve is changing less with time than the pressure curve. This probably indicates that in spreading at restricted areas there is an initial period in which the actual surface concentration of protein is changing, owing to translation

of protein chains along the surface, but that the later and longer period of the changes is due to readjustments similar to the equilibration at each step in compression.

The experiments here presented extend to low pressures the range of the metastable state given by Hughes and Rideal (6) for gliadin films. The importance for the theory of film structure of the independence of potential and pressure in the plateau region has been emphasized by ter Horst (5). The facts shown in the present experiments, that potential depends only partially upon the area of the film (or surface concentration) and not at all upon equilibration of pressure, must be taken into consideration in any general theory of film structure.

SUMMARY

The method of preparation of certain nerve protein fractions and the general features of the unimolecular films formed by them on various sub-solutions are described.

A phenomenon of pressure equilibration following change of area of these films has been observed. This equilibration is not associated with changes in phase boundary potentials and is distinct from irreversible collapse. The relation of this equilibration to film spreading at restricted areas is discussed.

REFERENCES

- (1) ASTBURY, W. T., DICKINSON, S., AND BAILEY, K.: *Biochem. J.* **29**, 2351 (1935).
- (2) DEVAUX, H.: *Compt. rend. soc. biol.* **119**, 1124 (1935).
- (3) FOURT, L., AND PERLEY, A. M.: *Proc. Soc. Exptl. Biol. Med.* **33**, 201 (1935).
- (4) GORTER, E., ORMONDT, H. V., AND MEIJER, T. M.: *Biochem. J.* **29**, 38 (1935).
- (5) TER HORST, M. G.: *Rec. trav. chim.* **55**, 33 (1936).
- (6) HUGHES, A. H., AND RIDEAL, E. K.: *Proc. Roy. Soc. London* **137A**, 62 (1932).
- (7) LEVENE, P. A.: *Arch. Neurol. Psychopathology* **2**, 1 (1899).
- (8) MORROW, C. A.: *Biochemical Laboratory Methods*. John Wiley and Sons, New York (1927).
- (9) SCHMITT, F. O., AND BEAR, R. S.: (a) *Proc. Soc. Exptl. Biol. Med.* **32**, 943 (1935); (b) *Am. J. Physiol.* **113**, 116 (1935).
- (10) SCHMITT, F. O., BEAR, R. S., AND CLARK, G. L.: *Radiology* **25**, 131 (1935).
- (11) YAMINS, H. G., AND ZISMAN, W. A.: *J. Chem. Physics* **1**, 656 (1933).

TRANSFERENCE NUMBERS OF COLLOIDAL "FERRIC HYDROXIDE"¹

JAMES W. MCBAIN AND WINIFRED McCLATCHIE THOMAS

Department of Chemistry, Stanford University, California

Received June 11, 1936

INTRODUCTION

It was demonstrated by Laing (2), in her work with soap solutions, that colloidal electrolytes and ordinary electrolytes show the same type of electrokinetic behavior, and hence can be studied by comparable experimental methods. "Ferric hydroxide" sols are typical charged colloids differing only in degree from typical colloidal electrolytes. It is therefore to be expected that their transference numbers can be measured by the same methods that are used for simple electrolytes, namely, the analytical method of Hittorf and the method of moving boundaries.

The identity of these two methods for measuring transference numbers was pointed out by Miller (8) and by Lewis (3), and was experimentally verified by MacInnes and his coworkers (4, 5). Many colloid chemists, however, have not recognized that this identity must also hold true for colloids. It was therefore desired to demonstrate this truth by experimental measurements on a typical charged colloid such as a "ferric hydroxide" sol.

The requirements for reliable Hittorf determinations of colloids have been clearly stated by Laing (2). The requirements for moving-boundary measurements of ordinary electrolytes have been established by MacInnes and his coworkers (5), but have been applied to colloidal solutions only by Robinson and Moilliet (9) in their study of dye solutions.

The following are the most important conditions that should be observed in any moving-boundary determination: The slower ion, usually the indicator, should follow; only the receding boundary should be observed; the denser solution should be on the bottom; the concentrations of the two ions forming the boundary should be approximately in the ratio $C/T = C^1/T^1$, where C and C^1 represent concentrations and T and T^1 represent transference numbers; the concentration of the indicator should preferably be slightly less than that indicated by the equation; a tube of small bore should be used; one electrode compartment should be closed; the electrode

¹ Presented at the Thirteenth Colloid Symposium, held at St. Louis, Missouri, June 11-13, 1936.

in the closed compartment should be reversible; and volume changes on the closed side of the boundary should be known.

Colloidal "ferric hydroxide" is a good material with which to demonstrate the fact that accurate transference measurements can be made by both the Hittorf and the moving-boundary methods. Moderately concentrated sols can be prepared, and they exhibit a conductivity comparable to that of dilute solutions of ordinary electrolytes. It is therefore possible to find an ion of lower mobility than the colloid to serve as an indicator. The only uncertain factor is the presence of small amounts of hydrogen ion in all "ferric hydroxide" sols. It is, however, probable that there would be no appreciable disturbance of the boundary if the same concentration of hydrogen ion were present in the indicator as in the sol.

EXPERIMENTAL

Hittorf determinations

These experiments were carried out on "sol 13," the properties of which have been recorded in two previous communications (6, 7).

The method used for Hittorf determinations was similar to that described by Laing (2). Figure 1 shows the transference cell. It was of Pyrex glass, and had a capacity of about 100 cc. The usual silver coulometer was not sufficiently sensitive to determine the current passed through the cell. The current density was therefore measured by means of a galvanometer that had been calibrated as a milliammeter. The total current was determined by plotting current density against time and taking the area under the curve. Four B-batteries in series (200 volts) supplied the current. All portions of the circuit were insulated from the ground.

In these gravimetric Hittorf measurements the sol was placed so as to fill the middle portion (tubes 3 and 4) completely, and to extend half way up in tubes 2 and 5. Then with the cell in position, a known weight of 0.0001 *N* sodium nitrate solution was introduced from a separatory funnel with flaring, upturned tip, to serve as a guard solution. This prevents contact with the electrodes and also provides definite electrode reactions not interfering with the analysis employed. Before starting a run, the cell was allowed fifteen minutes to attain the temperature of the thermostat, $25^{\circ} \pm 0.02^{\circ}\text{C}$. During a run the current density was measured every 5 minutes, and the zero point of the galvanometer was checked frequently. Three middle portions, "AM," "M," and "CM," and both electrode portions were analyzed for iron and chlorine according to the methods described in a previous communication (7).

The transference numbers of ferric oxide and of chlorine were calculated relative to water. The final weight of water in each electrode compartment was determined by subtracting the weight of guard solution and the

weight of ferric oxide found by analysis from the total weight of solution. The weights of ferric oxide and chlorine originally present were calculated from the composition of the sol.

The Hittorf migration results are given in table 1. The Hittorf number is defined as the number of chemical equivalents of the named constituent which pass from one electrode compartment to the other for each faraday (96,500 coulombs) of current passed through the solution. The middle portion remains unaltered in composition. For colloidal systems, as for electrolytes, the algebraic sum of the number of electrochemical equivalents or charges carried in the two directions must always add up to unity for each faraday of current passed. In the case of simple electrolytes carrying

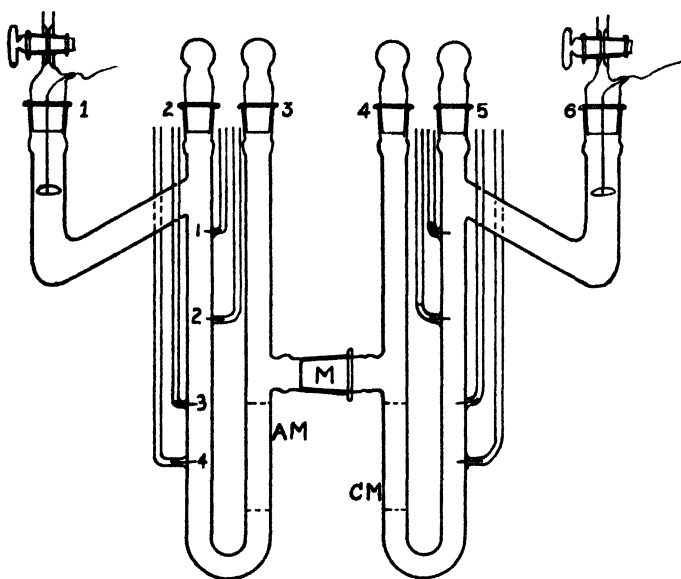


FIG. 1. Migration apparatus

one charge per chemical equivalent, the same statement holds true for chemical equivalents. However, since a colloid may carry many chemical equivalents per electrical charge, the Hittorf numbers may be greater than unity, as in table 1. Here the migration numbers appear as 70.3 equivalents of iron and 2.50 of chlorine for each faraday, both moving towards the cathode. Thus, 2.50 more equivalents of un-ionized chlorine is carried in the positive colloidal particles towards the cathode than is simultaneously carried toward the anode by the corresponding free chloride ions.

Moving-boundary determinations

The migration velocity of colloidal "ferric hydroxide" was measured in the same cell that was used for Hittorf determinations. The guard

solutions, now used as indicator solutions, were of lithium chloride, made to the same hydrogen-ion concentration as the sol with hydrochloric acid, and were equally conducting with the sol.

TABLE 1

Hittorf measurements of transference numbers expressed as chemical equivalents of iron and chlorine transported per faraday for "ferric hydroxide sol 18"

PORTION	TRANFERENCE OF $\text{Fe}(\text{OH})_3$		TRANFERENCE OF Cl	
	Change in equivalents	Hittorf number	Change in equivalents	Hittorf number
Experiment 1: current passed, 4.66×10^{-5} faradays				
A.....	-0.00329	70.6	-0.000116}	-2.51
AM.....	+0.00001		-0.000001}	
M.....	+0.00002}	69.6	+0.000003}	-2.51
CM.....	+0.00004}		+0.000002}	
C.....	+0.00318}		+0.000112}	
Average.....		+70.1		-2.51
Experiment 2: current passed, 3.45×10^{-5} faradays				
A.....	-0.00245	71.0	-0.0000873	-2.56
AM.....	+0.00002		-0.0000000	
M.....	+0.00001}	69.9	-0.0000007}	-2.43
CM.....	+0.00002}		+0.0000028}	
C.....	+0.00238}		+0.0000810}	
Average.....		+70.5		-2.50

TABLE 2

Moving-boundary measurements expressed as transference numbers and as absolute velocities, showing identity with results of Hittorf method for "ferric hydroxide sol 18"

Indicator solution: 7.5×10^{-4} N hydrochloric acid + 5.5×10^{-3} N lithium chloride

TIME	MOVEMENT OF BOUNDARY	POTENTIAL GRADIENT	MOBILITY	HITTORF NUMBER
minutes		volts/cm.	cm./sec./volt/cm.	
119	5.04	1.57	4.45×10^{-4}	70.3
90	3.75	1.51	4.58×10^{-4}	72.4
From Hittorf number, table 1.....			4.45×10^{-4}	70.3

($C = 0.933$ equiv. per liter on basis of analysis in Hittorf experiments.)

The potential gradient was determined by measuring the difference in potential between two of the platinum terminals shown in figure 1. The measurements were made by means of a Leeds and Northrup student

potentiometer and a high-sensitivity, high-resistance galvanometer. The method was checked by using a dilute potassium chloride solution in the cell, the potential gradients observed between different terminals checking within less than 1 per cent.

The boundaries between sol and guard were formed in the manner that was described for Hittorf determinations. The cell was allowed fifteen minutes to attain the temperature of the thermostat. The boundaries were observed by means of a traveling microscope. Their position, when first formed, could be read to within 0.2 to 0.4 mm. After the current had been passed for about fifteen minutes, the anode boundaries were read to within 0.1 mm. Observations of potential gradient and of boundary position were made about every 5 minutes during each run.

The transference numbers of iron obtained by this method for "sol 13" are summarized in table 2 for two independent experiments, involving twenty-seven readings. They were calculated from the equation

$$T = \frac{UFC}{1000K}$$

where T is the Hittorf number, U is the absolute velocity in cm. per second per volt per centimeter, F is Faraday's constant (96,500 coulombs), C is the concentration in chemical equivalents per liter, and K is the specific conductivity.

DISCUSSION OF RESULTS

These results definitely prove the possibility of measuring the transference numbers of charged colloids as well as colloidal electrolytes by both the analytical and the moving-boundary methods. The values obtained by the two methods agree within the experimental error of the moving-boundary measurements as made in these experiments. More accurate results could be obtained by more rigid adherence to the principles listed in the introduction.

The chief source of inaccuracy was in the use of an apparatus with both electrode compartments open, making the application of exact volume corrections impossible without further study (3). However, since the total current passed was very small, about 5×10^{-5} faradays, volume changes due to electrode reactions were practically negligible. The only appreciable errors were due, first, to the slight hydrostatic readjustment of the liquid boundary caused by the transference or displacement of the "ferric hydroxide" in density, and, secondly, to the slight volume changes accompanying the transference. This might make the results low by about 2 per cent.

A third source of error was due to the use of an indicator solution that was more concentrated than the required value, 4.2×10^{-3} , calculated from

$C/T = C^1/T^1$. However, it has been found (1) that the range of adjustment is relatively great for solutions of this dilution, so that the error was probably very slight and would tend to cancel the error due to transference of "ferric hydroxide."

COLLECTED PROPERTIES

A summary of the chemical and physical properties of "ferric hydroxide sol 13," as presented in this and two previous communications (6, 7), is given in table 3. The second column gives properties of the actual sol, containing both colloid and small amounts of free hydrochloric acid. The third column represents an "ideal" sol containing only the positive colloidal particles and the corresponding chloride ions. These values are obtained by correcting the values in column two for the effect of the ultrafiltrate.

TABLE 3

*Summary of properties of "ferric hydroxide sol 13" at 25°C.**

	ACTUAL SOL	"IDEAL" SOL
Equivalents of Fe per 1000 g. H ₂ O.....	0.934	0.934
Equivalents of Cl per 1000 g. H ₂ O.....	0.0449	0.0430
$C_{\pi+}$	6.3×10^{-5}	1×10^{-7}
Specific conductivity, in mhos.....	5.70×10^{-4}	5.40×10^{-4}
Hittorf number of Fe.....	70.3	74.2
Hittorf number of Cl (not Cl ⁻ only).....	-2.51	-2.65
Mobility of Fe in cm./sec./volt/cm.....	4.52×10^{-4}	4.52×10^{-4}
Mobility of Cl ⁻ in cm./sec./volt/cm.....	7.91×10^{-4}	7.91×10^{-4}
Equivalent of Fe per faraday of free charge†.	206	206
Concentration of free chloride ion†.....	0.0064	0.0045

* The diffusion coefficient of "sol 20" at 25°C. was found to be 0.613 as compared with 0.46 for sucrose by McBain, Dawson, and Barker (J. Am. Chem. Soc. **56**, 1021 (1934)).

† Calculation as given below.

The number of chemical equivalents of iron per faraday of free charge, m_{Fe} , was calculated by means of the Laing equation (2),

$$T_{Fe} = \frac{m_{Fe} f_{Fe} C_{Fe}}{\mu}$$

where T_{Fe} is the Hittorf number, 74.2, f_{Fe} is the conductivity contributed by one chemical equivalent, C_{Fe} is the concentration in chemical equivalents per 1000 g. of solvent, 0.934, and μ is the conductivity of that amount of solution containing 1000 g. of solvent, approximately $1000 \times 5.40 \times 10^{-4} = 0.540$ mho.

All the above quantities are experimentally determined except m_{Fe} and f_{Fe} . The latter can be eliminated by means of the independent equation,

$\mu = c_{Fe} f_{Fe} + C_{Cl-} v$, where C_{Cl-} is the concentration of free chloride ions and v their mobility. Solving for f_{Fe} and substituting $C_{Cl-} = c_{Fe}/m_{Fe}$ gives

$$f_{Fe} = \frac{\mu m_{Fe} - c_{Fe} v}{m_{Fe} c_{Fe}}$$

Substituting this in the Laing equation,

$$m_{Fe} = \frac{T_{Fe} \mu + c_{Fe} v}{\mu}$$

T_{Fe} is taken as the value for the "ideal" sol or 74.2, v is assumed to be the same as at infinite dilution or 76.3, and μ may be taken equal to $K \times 1000$ or 0.540. This gives $m_{Fe} = 206$. The corresponding concentration of chloride ion due to dissociation is $0.934/206 = 0.0045 N$. This free chloride ion, $0.0045 N Cl^-$, is only 10.5 per cent of the total chloride, $0.0430 N$, carried in the sol, the other 89.5 per cent being carried in the positive particle in undissociated unconducting form.

As compared with the equivalent conductivity of the free chloride ion, 76.3 mhos, the conductivity of one equivalent of positive charges carried on the positive particles is 43.6 mhos; hence that of the amount of charge carried by one chemical equivalent of iron is 206 times less, or 0.212 mho. A positive charge on the colloidal particle thus conducts 43.6/76.3, or 57 per cent as well as an ordinary chloride ion.

Finally the so-called zeta potentials, which, since they have never been measured directly are always calculated by multiplying the observed linear mobility by $4\pi\eta/D$ or 129,700, come out as +58.6 mv. for the positive colloidal particles and -102.6 mv. for the ordinary free chloride ions.

SUMMARY

The transference numbers of iron and chlorine in a "ferric hydroxide" sol were measured by the Hittorf and moving-boundary methods, which were found to give identical results within the limits of experimental error.²

The importance of making such measurements in accordance with methods established for use with simple electrolytes was pointed out.

The interesting and significant physicochemical properties of "sol 13," as reported in this and two previous communications, are summarized.

² Footnote added in proof: Roberts and Carruthers (J. Phys. Chem. 40, 703 (1936)) have now shown that the moving boundary and the observation of a single particle give identical results. This is inevitable, if electrode changes do not reach through the middle portion, since all movement is referred to motionless solvent. On the whole, apart from slight density changes outside the middle portion, the solvent does not move in either a closed or an open U-tube.

REFERENCES

- (1) HARTLEY, G. S., AND MOILLIET, J. L.: *Proc. Roy. Soc. London* **140A**, 141 (1923).
- (2) LAING, M. E.: *J. Phys. Chem.* **28**, 673 (1924); and a later more systematic study, *Trans. Faraday Soc.* **31**, 153 (1935); cf. MCBAIN, J. W.: *Acta Physico-chimica U. R. S. S.* **4**, 169 (1936).
- (3) LEWIS, G. N.: *J. Am. Chem. Soc.* **32**, 862 (1910).
- (4) LONGSWORTH, L. G.: *J. Am. Chem. Soc.* **54**, 2741 (1932).
- (5) MACINNES, D. A., AND LONGSWORTH, L. G.: *Chem. Rev.* **11**, 171 (1932).
- (6) MCBAIN, J. W., AND MCCLATCHIE, W. L.: *J. Am. Chem. Soc.* **55**, 1315 (1933).
- (7) MCCLATCHIE, W. L.: *J. Phys. Chem.* **36**, 2087 (1932).
- (8) MILLER, LASH: *Z. physik. Chem.* **69**, 436 (1909).
- (9) ROBINSON AND MOILLIET: *Proc. Roy. Soc. London* **143A**, 630 (1934).

A DIFFUSION STUDY OF DYES¹

SAMUEL LENHER AND J. EDWARD SMITH

Technical Laboratory, Organic Chemicals Department, E. I. du Pont de Nemours & Co., Inc., Wilmington, Delaware

Received June 11, 1936

The interest in the relationship of the substantive dyeing of cotton to the colloidal state of dyes in solution has led to extended investigations of the particle radius and the state of aggregation of representative water-soluble colors by Robinson and Mills (29), Ruggli and coworkers (34, 35), Haller (8), Schäffer (36), Schramek and Götte (37), Brass and Eisner (1), Rose (31), Valkó (40), the authors (14, 15, 16), and others. Diffusion measurements offer one of the simplest experimental approaches to a study of the colloidal state of dyes in solution. However, progress in the field has been slow because experimental methods were not well adapted to a study of dyes under actual dyeing conditions and because a suitable theoretical background for applying the measurements was lacking. Recent theoretical and experimental work of Hartley and Robinson (10), Bruins (2), and McBain (17, 18, 19, 20) and his coworkers has led to a correlation of the rate of diffusion of a colloidal electrolyte with the magnitude of the charge on the particle and the distribution of ions in the surrounding medium. The microdiffusion method of Fürth and Ullmann (4, 5) and the porous-plate method of Northrop and Anson (25) have been successfully applied in studies of colloidal electrolytes by Robinson (27, 28), Nistler (24), Schramek and Götte (37), McBain (17, 18, 19, 20) and his coworkers, and Valkó (40). The authors (14, 15) have recently applied both methods in a study of the diffusion of four chemically pure dyes. The dyes were as follows: (I) *p*-sulfobenzeneazobenzeneazo-6-benzoylamino-1-naphthol-3-sulfonic acid (sodium salt) (Colour Index No. 278); (II) *p*-sulfobenzeneazobenzeneazo-6-benzoyl-*p*-aminobenzoylamino-1-naphthol-3-sulfonic acid (sodium salt); (III) *o*-tolidinebisazo-1-naphthylamine-4-sulfonic acid (sodium salt) (benzopurpurin 4B, Colour Index No. 448); (IV) *m*-tolidinebisazo-1-naphthylamine-4-sulfonic acid (sodium salt) ("meta" benzo-purpurin 4B).

Dye I and dye II are of the same chemical type but possess widely different colloid-chemical properties. Dye I is characterized by its excel-

¹ Presented before the Thirteenth Colloid Symposium, held at St. Louis, Missouri, June 11-13, 1936.

lent level dyeing properties, poor fastness to washing, and poor exhaust from the dye bath on cotton. Dye II, in contrast, is more difficult to dye level and shows superior wash fastness as well as a high exhaust from the dye bath. The identifying difference in the formulas of dye I and dye II is the presence of a second benzoyl group in dye II. Dye III and dye IV are of another chemical type and differ between themselves only in the position of the methyl groups of the tolidine nucleus. The spatial change in the position of the methyl groups is associated with a great difference in the substantivity of the dyestuffs toward cotton.

The microdiffusion method used in this work was essentially the same as that of Fürth (4), and has been described by the authors (16). For most measurements, the microdiffusion cell was housed in an air thermostat whose temperature was held with a maximum variation of $\pm 0.5^\circ\text{C}$.

The porous-plate method was applied as described by McBain and Liu (20). Its adaptation to dyestuff measurements was described by the authors (14).

The dyes used in this work were prepared from purified intermediates by methods in current use for manufacturing azo colors. The dyes were freed of electrolytes by the method of Rose (32, 33). This method (14, 15) consists in converting the dyes to their arylguanidine salts (preferably di-*o*-tolylguanidine), which are insoluble in water. The dyes are washed free of inorganic electrolytes, are dissolved in alcohol, and are converted by metathesis with sodium hydroxide to the sodium salts. The precipitated sodium salts of the dyes are filtered and washed free of the arylguanidine with alcohol.

I. DIFFUSION AND AGGREGATION OF PURE DYES IN WATER

Herzog and Polotsky (12) showed that some purified dyes diffuse as electrolytes; Freundlich (3), Svedberg (38), and Tiselius (39) have pointed out the necessity of considering ionic forces in dealing with diffusion and sedimentation phenomena. Despite these facts the Stokes-Einstein equation

$$D = \frac{RT}{N} \cdot \frac{1}{6\pi\eta r} \quad (1)$$

has been applied indiscriminately for the calculation of the particle radius of dyes in solution until the recent theoretical treatment of Hartley and Robinson (10), who showed that theoretically the minimum diffusion constants for a number of dyes would be approximately 5.1×10^{-6} cm.² per second. Robinson (27) has demonstrated that representative purified dyes diffuse at an appreciably greater rate than the theoretical minimum (see table 1). Valkó (40) estimated that dyes which are the sodium salts of monobasic or dibasic acids may diffuse at rates as high as 7.2 to $8.2 \times$

10^{-6} cm.² per second. The data of Valkó on the diffusion of a number of representative pure dyes are of the same order. The authors obtained values of 8.8 to 9.0×10^{-6} cm.² per second for the diffusion of dye I and a value of 7.7×10^{-6} cm.² per second for the diffusion of dye II in water solution. These last values are about double those required for diffusion of the molecularly dissolved dye according to the Stokes-Einstein equation.

TABLE 1
Diffusion coefficients of pure dyes at 25°C.

DYE	MEASUREMENTS BY	CONCENTRATION RANGE	$D \times 10^{-6}$
		grams per liter	cm. ² per second
Orange II, C.I. 151.	Valkó	1 0-15 6	6 68-7 99
Azogrenadine S, C.I. 54 . . .	Valkó	0 5-5 0	8 38-7 86
Bordeaux Extra, C.I. 385 . . .	Robinson	0 8-2 5	5 42-5 66
Congo rubin, C.I. 376	Robinson	5 0	5 51-5 59
Congo red, C.I. 370	Valkó	0 1-5 0	6 63-7 73
Congo red, C.I. 370	Robinson	5 0	5 68
Benzopurpurin 4B, C.I. 448..	Valkó	0 2-5 0	6.12-7 48
Benzopurpurin 4B, C.I. 448. . .	Robinson	5 0	6 57
"Meta" benzopurpurin	Robinson	5 0	5 43-5 91
Dye I, C.I. 278	Lenher and Smith	0 5-1 0	8.84-9 01
Dye II.	Lenher and Smith	0 5	7.73

TABLE 2
Diffusion rate of dyes I and II into water and into dilute sodium chloride solutions at 25°C.

DYE	CONCENTRATION	DIFFUSING INTO NaCl SOLUTION	$D \times 10^{-6}$	CALCULATED PARTICLE WEIGHT
	grams per liter	grams per liter	cm. ² per second	
I	0 5		9 01	80
	0 5	0 087	3 84	1100
	1.0		8 84	90
	1 0	0 174	4.07	924
	1 0	0 500	3 10	2095
II	0.5		7.73	120
	0.45	0.074	4 21	770
	0 45	0.067	2.93	2280

The results for Congo red and benzopurpurin 4B in table 1 are considerably higher than a number of determinations reported by previous investigators (1, 5, 12, 24). The difference in the rate of diffusion is probably due to differences in the degree of purity of the dyestuffs, for both dyes are highly susceptible to aggregation in the presence of inorganic salts.

Hartley and Robinson (10) and Valkó (40) are agreed that, even after

the effect of the charge on the ions is considered, it is not possible to determine the state of aggregation of a pure dye in water solution from diffusion measurements. Hartley and Robinson (10) explain the high rate of diffusion of the color ion in solution as due to its attraction for the highly mobile sodium ion, i.e., both ions must diffuse into water at the same rate. It appears that for a completely dissociated dye, electroneutrality of the color ion with respect to the sodium ion in the diffusion cell would be established by carrying out the diffusion of the dye into an electrolyte solution containing an equivalent concentration of the metal ion. The authors studied this effect by determining the rate of diffusion of the sodium salt of dye I and dye II into dilute sodium chloride solutions. The measurements were made in the Fürth microdiffusion cell at 25°C. The data are summarized in table 2.

In table 2 the particle radius is calculated from equation 1. It is assumed that the dye molecules or micelles are large in comparison with the solvent and that they are spherical. Herzog, Illig, and Kudar (11) showed that the error caused by assuming the particles to be spheres is relatively small except in cases involving extreme elongation. The authors (16) have shown that the ultramicros of most dyes in sodium chloride solutions are practically spheres. The particle weight is calculated from equation 2 where the specific gravity (g) is 1.72 for dye I and 1.58 for dye II.

$$m = \frac{4}{3} \pi r^3 g N \quad (2)$$

The substitution in equation 1, and indirectly in equation 2, of the diffusion constants of dye I and dye II into water gives particle weights which are small fractions of the formula molecular weights, as is to be expected on theoretical grounds. The rate of diffusion of dye I into an equivalent concentration of sodium chloride gives particle weights of 900 to 1100 as compared with an ion weight of 629. The agreement is considered remarkably good, since the experimental error in the microdiffusion method is at least 5 per cent. An error of this magnitude might account for about half the difference between the calculated particle weight and the ion weight. In addition, the density of the dye particles in solution is not accurately known. The data indicate that the chloride ions from the salt solution diffusing in the opposite direction have very little effect on the rate of diffusion of the color ions. It appears that the negatively charged dye ion diffuses as a neutral particle in the presence of a uniform distribution of a common positive ion in the cell. The data of table 2 show that the rate of diffusion of dye I into a sodium chloride solution of three times the equivalent concentration is further retarded, as would be expected, since the diffusion occurs against a concentration gradient of sodium ions.

The value of D for the diffusion of dye II into an equivalent concen-

tration of sodium chloride also corresponds to that expected for the molecular diffusion of a neutral particle. However, diffusion into a higher salt concentration is accompanied by boundary disturbances, while the diffusion rate into a slightly lower (10 per cent) concentration of sodium chloride is, contrary to expectations, about 30 per cent lower. It appears that the distribution of positive and negative ions in a solution of dye II does not correspond to that of a molecularly dissolved, completely ionized dyestuff. The differences in the behavior of dye I and dye II in these experiments indicate that dye I closely approaches the molecular state in solution, while dye II is aggregated into micelles.

The successful application of the above method to dye I and dye II suggests that it is possible to determine whether water-soluble dyes are in true solution by observing the rate of diffusion into an equivalent concentration of sodium chloride.

II. DIFFUSION AND AGGREGATION OF DYES IN SALT SOLUTIONS

The necessary conditions for determining diffusion constants that may be substituted in the Stokes-Einstein equation to estimate the particle radius of dyes in solutions containing inorganic electrolytes have been considered recently in a number of papers. Hartley and Robinson (10) and Valkó (40) are of the opinion that diffusion experiments with dyes must be carried out in the presence of a uniform concentration of a foreign electrolyte to permit application of the diffusion constants in the Stokes-Einstein equation for the determination of the particle radius. The authors (14, 15) were unable to apply this principle in a study of dye I and dye II because of boundary disturbances which occurred in the micro-diffusion cell. The same trouble was experienced by Robinson (27) with dye IV, but only at relatively high (0.25 *N*) concentrations of sodium chloride. If a uniform concentration of the foreign electrolyte were required, it would be expected that the diffusion rate of the dye would increase when diffusion occurs into a sodium chloride solution of lower concentration than that present in the dye solution, and that a further increase would occur for diffusion of the dye from the salt solution into water. The authors (14) tested this theory by measuring the rate of diffusion of dye I and dye II from a solution containing 1.0 g. of sodium chloride per liter into water and into a solution containing 0.5 g. of sodium chloride per liter. The data are given in table 3.

Practically identical diffusion constants were obtained for the movement of the color ion from a sodium chloride solution into water, and for diffusion into a sodium chloride solution of half concentration. Robinson (27) obtained practically identical diffusion constants for the diffusion of dye IV from a 0.004 *N* (0.232 g. per liter) sodium chloride solution into water and into a 0.004 *N* sodium chloride solution. It is apparent, from these

data, that the rate of diffusion of the ordinary water-soluble dyes from a salt solution whose concentration is 0.02 *N*, and possibly as low as 0.004 *N*, into water is the same as the rate of diffusion into salt solutions of the same or lower concentrations. It is apparent that the diffusion of sodium ions from these solutions is accompanied by movement of the highly mobile chloride ions in quantities that prevent the establishment of a potential gradient between the sodium and dye ions. The data show that the only requirement for independent diffusion of the dye ion, in a manner analogous to the diffusion of an electrically neutral particle, is the presence of several times the equivalent concentration of sodium chloride in the dye solution. The diffusion rate of the dye ion from a salt solution into either water or another salt solution represents the normal independent diffusion rate of the dye ion.

TABLE 3
Diffusion of dye I and dye II in the presence of electrolytes

DYE	SOLUTION		AGE OF SOLUTION	DIFFUSION INTO NaCl SOLUTION	$D \times 10^{-4}$
	Dye + NaCl				
	grams per liter	grams per liter			
I	0.5	1.0	168		2.38
I	0.5	1.0	168	0.5	2.45
I	1.0	1.0	90		2.31
I	1.0	1.0	90	0.5	2.40
II	0.5	1.0	48		0.94
II	0.5	1.0	72	0.5	0.93
II	1.0	1.0	336		0.96
II	1.0	1.0	312	0.5	1.04

III. AGING PHENOMENA OF DYES IN SALT SOLUTIONS

The degree of aggregation of a dye in solution frequently varies with the age of the solution. Experiments with dye I (summarized in table 4) show that particle growth at room temperature occupies several days. The particle weight in a solution containing 1.0 g. of sodium chloride per liter increased by 30 per cent on aging from two days to a week, and was practically doubled on aging for a month. The maximum aggregation with dye II in a salt solution is reached within a few hours.

Solutions of dye I containing sodium chloride, on aging for several weeks, develop abnormal diffusion properties as compared with fresh solutions. In these experiments solutions containing from 0.5 to 1.0 g. of dye per liter and 1.0 g. of sodium chloride per liter were aged forty-eight to ninety hours at room temperature. The diffusion rates of the color ion into water and into sodium chloride at concentrations up to 0.5 g. per liter were practically the same. Similar dye solutions were prepared and aged for four weeks.

It was found on measuring the diffusion rate of the color ion into water and into sodium chloride solutions (0.125 to 0.5 g. per liter) that a measurable accelerated diffusion occurred into the salt solutions. The data are summarized in table 4.

In table 4 each figure given represents at least two individual diffusion experiments in each of which at least eight determinations were made during a period of twenty to thirty minutes.

The data in table 4 show that diffusion of the color ion from the aged dye solution into the salt solution became more highly accelerated the

TABLE 4
Diffusion properties of aged dye solutions

DYE	CONCENTRATION		AGE OF SOLUTION	T	DIFFUSION INTO NaCl	D × 10 ⁻⁴
	Dye	+ NaCl				
	grams per liter	grams per liter		°C.	grams per liter	cm. ³ per second
I	0.5	1.0	2 days	29		3.13
I	0.5	1.0	2 days	30	0.5	3.22
I	0.5	1.0	1 week	30		2.66
I	0.5	1.0	1 week	28	0.5	2.62
I	0.5	1.0	3.5 weeks	25		2.13
I	0.5	1.0	3 5 weeks	26	0.125	2.58
I	0.5	1.0	3.5 weeks	25	0.25	2.96
I	0.5	1.0	3 5 weeks	26	0.5	3.18
I*	0.5	2.0	3.5 weeks	26		2.17
I*	0.5	2.0	3.5 weeks	26	1.0	2.08
I	1.0	1.0	4 days	27		2.46
I	1.0	1.0	4 days	27	0.5	2.40
I	1.0	1.0	4 weeks	29		2.14
I	1.0	1.0	4 weeks	30	0.25	2.67
I	1.0	1.0	4 weeks	30	0.5	3.03

* This solution was dye I, 0.5 g. per liter, plus sodium chloride, 1.0 g. per liter, aged for 3.5 weeks. Then sodium chloride was added to make the salt concentration 2.0 g. per liter, and the measurements were made with this solution immediately.

greater the sodium-ion concentration of the solution into which diffusion occurred. When more sodium chloride was added to the dye solution and the diffusion of the color ion was measured into water and into a salt solution, as indicated, no acceleration in the diffusion rate was observed, i.e., diffusion occurred in the normal manner.

The mechanism of the change in properties of the dye solution is not understood. It appears that the accelerated diffusion can be accounted for only on the basis of the presence of an ionic gradient between the dye and the salt, since the diffusion rate varies with the concentration of sodium ions in the solution into which diffusion occurs.

IV. DEPENDENCE OF DYE PARTICLE SIZE ON SALT CONCENTRATION AND TEMPERATURE

The effect of electrolyte concentration and of temperature on the degree of aggregation of dyes in solution is of great practical importance, since the size of the dye micelle is a controlling factor in dyeing processes.

The preceding résumé shows that the diffusion rate of dyes from solutions containing an inorganic electrolyte, as sodium chloride, into either water or any concentration of the electrolyte up to that present in the dye solution may be used to calculate the particle radius from equation 1. The history of the dye solution must be known to establish accurately the

TABLE 5

Effect of sodium chloride on colloidal state of dyes in solution at 25°C.

DYESTUFF	CONCENTRATION	CONCENTRATION OF NaCl	$D \times 10^{-3}$	$R \times 10^{-6}$	PARTICLE WEIGHT	AGGREGATION NO.
	<i>grams per liter</i>	<i>N</i>	<i>cm.² per second</i>	<i>cm.</i>		
Orange II, C.I. 151.....	0.05-0.1	0.02	5.10	4.77	413	1 2
	0.2	0.05-0.2	4.05	5.74	564	1.7
Azogrenadine S, C.I. 54..	0.05-0.5	0.02-0.05	4.74	5.12	511	1 1
	1.0	0.1	3.82	6.35	976	2 1
Benzopurpurin 4B, C.I. 448....	0.02-0.1	0.01-0.02	2.43	10.0	3810	5.6
	0.05-0.2	0.02	2.08	11.7	6100	9.0
Congo red, C.I. 370.....	0.05-0.1	0.02-0.05	1.85	13.1	8560	12.0
	0.5	0.1	1.50	16.2	16200	24.0
Chicago blue 6B, C.I. 518.....	0.02-0.2	0.02-0.05	2.55	9.55	3310	3.7
	0.2	0.1	2.08	11.7	6100	6 8
	0.2	0.2	1.62	15.0	12800	14.0
	0.2	0.5	1.39	17.5	20400	23.0

effect of electrolyte additions, since the state of aggregation may depend on the age of the solution. Extended aging may introduce complications due to acceleration of the diffusion rate into salt solutions.

Valkó (40) studied the effect of varying salt concentrations on the rate of diffusion of two acid dyes and three substantive dyes by the porous-plate method. Part of the data are summarized in table 5.

The data show that the acid dyes are in molecular solution at salt concentrations up to 0.02 *N*, while the substantive dyes are aggregated into micelles. The acid dyes in solution are much less readily agglomerated by additions of sodium chloride than are the substantive dyes. However, in all cases there is an increase in the degree of aggregation of the dyes at sufficiently high concentrations of sodium chloride.

Brass and Eisner (1) reported on the basis of diffusion measurements that the particle size of pure dyes in solution is much smaller than the particle size of unpurified samples.

Schramek and Götte (37) studied the effect of various electrolytes on the degree of dispersion of two substantive dyes (C. I. 385, C. I. 390) in water solution by the Fürth (4) method. Their values for the rate of diffusion of the pure dyes in water are much lower than would be expected.

TABLE 6
Agglomeration of dyes by electrolytes at 25°C.

SOLUTION OF				$D \times 10^{-6}$	ESTIMATED RADIUS $R \times 10^{-8}$	PARTICLE WEIGHT (m)	AGGREGA- TION NO.
Dye	+	NaCl	+ Na ₂ SO ₄				
	<i>grams per liter</i>	<i>N</i>	<i>N</i>	<i>cm.² per second</i>	<i>cm.</i>		
Dye I	0.5	0.027		2.08	11.7	6990	11
	0.5		0.027	3.19	7.6	1920	3
	0.5	0.107		1.52	16.0	17900	28
	0.5		0.107	2.50	9.7	3990	6
Dye II	0.5	0.027		0.71	33.7	153500	205
	0.5		0.027	1.32	18.4	25000	33
	0.5	0.107		0.72	34.2	160400	214
	0.5		0.107	1.60	15.2	14100	19
Dye III	1.0	0.01		2.69	9.0	2800	4
	1.0		0.01	4.52	5.4	605	0.9
	1.0	0.025		0.92	26.4	71000	105
	1.0		0.025	1.91	12.7	7900	12
	1.0	0.05		0.39	62.2	928000	1370
	1.0		0.05	0.75	32.3	130000	190
	1.0	0.01		2.99	8.1	2160	3.2
	1.0		0.01	4.45	5.5	675	1.0
	1.0	0.025		2.02	12.0	7020	10
	1.0	0.05		2.06	11.8	6675	10
	1.0		0.05	4.20	5.8	790	1.2
	1.0	0.1		1.64	14.8	13170	19
	1.0		0.1	3.49	7.0	1390	2.1

They found that additions of sodium chloride, sodium sulfate, sodium carbonate, and magnesium sulfate all act at low concentrations to disperse the dyes, and at higher concentrations as agglomerating agents. A dispersing action of small additions of sodium sulfate on pure dyes in solution was also reported by Ostwald (26).

The authors (14, 15) used the microdiffusion method to determine the rate of diffusion of dyes I, II, III, and IV in the presence of electrolytes at 25°C. The dye solutions were prepared at the boil and aged at 25°C.

for eighteen hours before the measurements were made. The diffusion rate was measured from the electrolyte solution into water. There was no indication that the concentration of inorganic electrolyte in the dye solution changed sufficiently during the short diffusion period of twenty to thirty minutes to cause a change in the colloidal state of the dye during measurements. The data are summarized in table 6.

The data in table 6 show that the four dyes are characteristically different in the extent to which they are agglomerated by electrolyte additions. Dye II and particularly dye III are highly sensitive to additions of sodium chloride and sodium sulfate. Dye I and dye IV are much less aggregated, especially in the presence of sodium sulfate. In general, sodium chloride exerts an appreciably stronger agglomerating action than does sodium sulfate with corresponding dyestuffs.

Robinson (27) showed, from measurements by the microdiffusion method, that benzopurpurin 4B (C. I. 448) and Congo red (C. I. 370) are considerably more highly aggregated by sodium chloride than either Bordeaux Extra (C. I. 385) or "meta" benzopurpurin. He found that the diffusion constants of Bordeaux Extra and "meta" benzopurpurin, obtained in the presence of increasing salt concentrations, fall to a constant minimum for both dyes. The minimum diffusion constant for Bordeaux Extra in salt solutions corresponds approximately to that for a molecular solution, and it is inferred that the dye is in the molecular state in water. The minimum diffusion constant for "meta" benzopurpurin in salt solutions shows that the dye is associated into micelles of more than ten molecules. Robinson (27) has interpreted the data as showing that the dye is also in the form of micelles of more than ten molecules in water solution. As Robinson (27) points out, this extrapolation gives a result which is in agreement with osmotic-pressure measurements, but is too high in comparison with the mobility measurements of Robinson and Moilliet (30). Such an extrapolation of the data appears hazardous, in view of the ease with which dyes are aggregated in dilute solutions of electrolytes. The data of table 6 show that diffusion constants for "meta" benzopurpurin (dye IV) in the presence of sodium sulfate are much higher than at equivalent concentrations of sodium chloride. It is shown that dye IV is in the molecular state in sodium sulfate solutions up to 0.05 *N*, and it is inferred that the dye is in true solution in the absence of electrolytes. These results correspond more nearly to the state of aggregation for "meta" benzopurpurin (1.2) deduced by Robinson and Moilliet (30) from mobility experiments. The data of table 6 also show that benzopurpurin 4B (dye III) is in the molecular state in 0.01 *N* sodium sulfate solution, and it is inferred that the dye is in true solution in water. Robinson and Moilliet (30) found from mobility experiments that the degree of aggregation of benzopurpurin 4B in solution is 1.5. It appears that the differ-

ences in the colloid-chemical properties of benzopurpurin 4B and its isomer arise from the great difference in the sensitivity of the two dyes to agglomeration by inorganic salts, rather than from a large difference in the state of the pure dyes in water solution.

The data of Valkó (40), Robinson (27), and the authors (14, 15) show that the only effect of the addition of sodium chloride and sodium sulfate to a number of representative dyes is to increase the particle size of the dyes in solution. As pointed out above, Schramek and Götte (37) found that low concentrations of electrolytes first disperse some dyes and that greater concentrations produce reagglomeration. The wide variation between the diffusion constants of the pure dyes of Robinson (27), Valkó (40), and the authors (14) compared with the diffusion constants for the dyes of Schramek and Götte (37) suggest that the widely different methods of purification give dyes of a different degree of purity. The conflicting results from diffusion measurements made in solutions containing low concentrations of electrolytes are probably due to a difference in the degree of purity of the dyes.

It has been commonly recognized that increased temperatures lead to increased dispersion of dyes in colloidal solution. The authors (14, 15) made a quantitative study of the effect of temperature on the degree of dispersion of dyes I, II, III, and IV in electrolyte solution by carrying out diffusion measurements with the porous-plate type of cell. In these experiments the diffusion of the dye was carried out from a salt solution into another salt solution of equal concentration. Quantitative observations of the increase in the dispersion of the dyes with increase in the temperature are summarized in table 7.

The particle weights were calculated by equation 2, using the following experimentally determined values of g : dye I, 1.72; dye II, 1.58; dye III, 1.52; dye IV, 1.60.

The data in table 7 show that while a general decrease in the degree of aggregation of dyes occurs with increasing temperatures, specific differences in behavior occur. Dyes I and IV are only slightly aggregated in 0.1 N sodium sulfate solutions; the average particle weights in 0.1 N sodium chloride solutions are less than 18,000. On raising the temperature to 94°C. the two dyes are dispersed to aggregates of average particle weight less than 3500. Dye III is precipitated in either 0.05 N sodium chloride or 0.05 N sodium sulfate solution at 25°C., and is partially precipitated in 0.075 N sodium chloride or 0.075 N sodium sulfate at 50°C. At 65°C. the dye is dispersed into aggregates of particle weight about 15,000 in 0.1 N sodium chloride, while at 95°C. the average particle weight is decreased below 2000. Dye II appears completely dissolved in a 0.1 N sodium chloride solution at 25°C. Diffusion measurements show that the dye is aggregated into micelles of a particle weight of at least 60,000. The

micelles remain unchanged at temperatures up to 65°C. At 80°C. dispersion is well under way, and at 95°C. the average particle weight is reduced to less than 5000. Experiments with dyes III and IV show that sodium chloride is a stronger agglomerating agent than sodium sulfate at elevated temperatures as well as at room temperature.

TABLE 7

Effect of temperature on aggregation of dyes in presence of electrolytes

DYE	DYE CONCENTRATION	ELECTROLYTE	ELECTROLYTE CONCENTRATION	T	$D \times 10^{-4}$	$R \times 10^{-4}$	PARTICLE WEIGHT (m)	AGGREGATION NO.
	grams per liter		N	°C.	cm. ² per second	cm.		
I	0.5	NaCl	0.107	25.0	1.52	16.0	17880	28
	1.0		0.107	50.1	3.10	13.7	11220	18
	1.0		0.107	65.8	5.61	10.2	4630	7.4
	1.0		0.107	80.0	7.10	9.3	3510	5.5
	1.0		0.107	95.5	10.05	9.0	3180	5.0
II	0.5	NaCl	0.107	25.1	0.96	25.3	64950	87
	1.0		0.107	50.1	1.75	24.6	59700	80
	1.0		0.107	65.5	2.26	25.2	64180	86
	1.0		0.107	80.6	3.86	18.8	26650	36
	1.0		0.107	95.4	7.80	11.3	5790	7.7
III	1.0	NaCl	0.01	50.5	5.25	8.2	2120	3.1
	1.0		0.025	50.5	4.3	10.0	3860	5.7
	1.0		0.05	50.5	3.35	12.9	8280	12
	1.0		0.075*	50.5	1.19*	36.3	184500	272
	1.0		0.05	65.2	5.32	10.6	4590	6.8
	1.0		0.10	65.2	3.5	16.2	16400	24
	1.0		0.10	94.2	10.92	8.1	2050	3.0
III	1.0	Na ₂ SO ₄	0.05	50.5	4.09	10.6	4590	6.8
	1.0		0.075*	50.5	1.28*	33.8	148700	219
	1.0		0.05	65.2	5.76	9.8	3630	5.4
	1.0		0.10	65.2	4.83	11.7	6180	9.1
	1.0		0.10	94.2	11.62	7.6	1690	2.5
IV	1.0	NaCl	0.1	94.2	11.8	7.5	1710	2.5
	1.0	Na ₂ SO ₄	0.1	94.2	12.88	6.9	1330	2.0

* Dye partially precipitated in cell.

The data presented show that with the possible exception of dye II, the representative acid and substantive dyes studied by a number of workers are close to the molecular state in solution in the absence of electrolytes. The addition of inorganic electrolytes agglomerates both types of colors; substantive dyes are much more strongly aggregated than are acid dyes

at the same salt concentrations. Elevation of the temperature disperses the dye micelles. Data on technical dyestuffs (16) show that a number of strongly substantive dyes are aggregated to micelles of at least one hundred molecules in 0.1 *N* sodium chloride. The data of this paper indicate that the degree of aggregation of substantive dyes in 0.1 *N* sodium chloride at the boil is less than ten molecules per micelle, and that in most cases the dyes approach the molecular state under practical dyeing conditions.

V. RELATION OF PARTICLE SIZE TO SUBSTANTIVITY OF DYES

It is well established that electrolyte-free cellulose has very little affinity for chemically pure dyes. The addition of an inorganic electrolyte, as sodium chloride, is required to promote the adsorption of dyes on cotton and rayon. The relative importance of the salt on the electrokinetic as compared with the mechanical factors in the dyeing process has been a source of extended experimentation and speculation.

Schäffer (36) states that a particle diameter of 4.5 millicrons represents the limiting size above which dyeing does not occur on cotton. The authors (16) showed from a study of the properties of twelve technical substantive dyes that dyeing at 25°C. on cotton does not progress readily unless the radius of the dye particles is less than 18×10^{-8} cm. Further studies (14, 15) were made with purified dyes. Dye I and dye II offer an interesting comparison, since they are markedly different in their dyeing properties and colloidal characteristics. The average particle radius of dye I in a dye bath containing 6.25 g. of sodium chloride per liter is less than 18×10^{-8} cm. (the estimated maximum for dyeing) over the temperature range 25° to 95°C. Dye II in a similar dye bath remains aggregated to particles of average radius greater than 18×10^{-8} cm. at temperatures up to 65°C. and possibly to 80°C. The particle radius rapidly decreases above 80°C. In dyeing experiments carried out to equilibrium, dye I is adsorbed by cotton most heavily at 25°C.; the degree of adsorption of dye I at the boil is only 40 per cent as great. Dye II is adsorbed by cotton from the dye bath very much less at temperatures below 65°C. than at temperatures greater than 80°C. Approximately four times as much of dye II is adsorbed at the boil as at 25°C. Rapid adsorption of dye II occurs only at temperatures above 75° to 80°C., i.e., at temperatures sufficiently great to disperse the dye to aggregates smaller than the maximum size for dyeing. The data are interpreted as showing that the highly salt-sensitive dye II is much more substantive to cotton than dye I. Marked adsorption of dye II is not obtained unless the proper degree of dispersion in the dye bath is obtained to permit penetration of the dye particles into the intermicellar spaces of the cotton.

Dyeing experiments were carried out with dye III and dye IV in which

comparisons were made of the degree of adsorption of the dye by cotton at the end of one hour. The dye baths contained varying concentrations of sodium chloride and sodium sulfate up to 0.2 *N*, while the temperatures were 25°, 50°, and 100°C. The data obtained show that the marked differences in the degree of aggregation of dye III and dye IV in salt solutions are reflected in the dyeing process. Adsorption of dye IV, whose average particle radius is always well below 18×10^{-8} cm., increases with increasing electrolyte concentrations and decreasing temperatures. In contrast, with dye III an optimum concentration of electrolyte exists above which the rate of adsorption is decreased at 25° to 50°C. This decrease, occurring at a 0.05 *N* salt concentration at 25°C. and a 0.075 *N* salt concentration at 50°C., corresponds with the attainment of an average particle radius in the dye bath greater than 18×10^{-8} cm.

Neale (6, 7, 9, 22, 23) and his coworkers have shown with a number of substantive colors that increasing concentrations of salt in the dye bath increase the absorption of dye, while increasing temperatures decrease the absorption of dye by cellulose at equilibrium. It is the point of view of the authors that these generalizations hold true only if the average particle size of the dye micelles in the dye bath permits penetration into the intermicellar spaces of the cotton. An average micellar radius greater than 18×10^{-8} cm. may act to retard the rate of dyeing without affecting the degree of adsorption at equilibrium, or it may inhibit dyeing to produce appreciably weaker dyeings. For example, a dye-bath of dye III containing 0.075 *N* sodium chloride at 50°C. is 95 per cent exhausted on cotton in one hour. At this concentration of salt the dye is partially precipitated from the bath and the average particle radius is 36×10^{-8} cm. This average particle radius for the dye in a bath which is partially flocculated indicates that a portion of the micelles is present as particles of radius less than 18×10^{-8} cm. It is inferred that as the micelles in the dyeing range are adsorbed, the larger micelles disperse to maintain the distribution of particles in the bath; and that the dyeing process is continued in this manner until the bath is exhausted. Morton (21) reached the same conclusion for other dyes from a different experimental basis. Dye II, in contrast to dye III, is not heavily adsorbed from the bath even after three weeks, unless the average particle radius is below the estimated maximum. Adsorption of substantive dyes by cotton from a bath containing micelles of an average particle radius greater than the maximum is either retarded or partially prevented, depending on the size distribution of the particles which go to make up the average radius and the rapidity with which this distribution is reestablished when it is disturbed by the adsorption processes occurring during the dyeing of cellulose.

All recent evidence shows that excellent dyeing with substantive colors on cotton may be obtained from baths containing micelles of any average

radius below the estimated maximum. The data do not support a mechanical theory of dyeing; micelles of the same average radius in the dye bath vary widely in their dyeing characteristics. Since practical experience has shown that temperatures near the boil are best for dyeing substantive dyes for cellulose, it is probable that the best levelness and penetration in practical dyeing processes is obtained when the particle size of the micelles is nearest the molecular state.

The evidence presented in this paper shows that the substantivity of the dye molecule for cotton is qualitatively related to its salt sensitivity. The degree of adsorption of substantive dyes at the boil increases, and the ease of reversibility of the dyeing process decreases with increasing salt sensitivity. It is probable that the same forces which lead to an agglomeration of molecules of substantive dyes into micelles are instrumental in causing adsorption of the dye by cellulose.

REFERENCES

- (1) BRASS, K., AND EISNER, K.: *Kolloid-Beihefte* **37**, 56 (1932).
- (2) BRUNS, H. R.: *Kolloid-Z.* **54**, 272 (1931); **57**, 152 (1931); **59**, 263 (1932).
- (3) FREUNDLICH, H.: *Colloid and Capillary Chemistry*, p. 547. E. P. Dutton and Co., New York (1922).
- (4) FÜRTH, R.: *Kolloid-Z.* **41**, 300 (1927).
- (5) FÜRTH, R., AND ULLMANN, E.: *Kolloid-Z.* **41**, 304 (1927).
- (6) GARVIE, W. H., GRIFFITHS, L. H., AND NEALE, S. M.: *Trans. Faraday Soc.* **30**, 271 (1934).
- (7) GRIFFITHS, L. H., AND NEALE, S. M.: *Trans. Faraday Soc.* **30**, 395 (1934).
- (8) HALLER, R.: *Kolloid-Z.* **11**, 110 (1912); **13**, 255 (1913); **20**, 127 (1917); **23**, 100 (1918); **29**, 95 (1921).
- (9) HANSON, J., AND NEALE, S. M.: *Trans. Faraday Soc.* **30**, 386 (1934).
- (10) HARTLEY, G. S., AND ROBINSON, C.: *Proc. Roy. Soc. London* **134A**, 20 (1931).
- (11) HERZOG, R. O., ILLIG, R., AND KUDAR, H.: *Z. physik. Chem.* **167A**, 329 (1934).
- (12) HERZOG, R. O., AND POLOTSKY, A.: *Z. physik. Chem.* **87A**, 449 (1914).
- (13) LENHER, S., AND SMITH, J. E.: *J. Am. Chem. Soc.* **56**, 999 (1934).
- (14) LENHER, S., AND SMITH, J. E.: *J. Am. Chem. Soc.* **57**, 497 (1935).
- (15) LENHER, S., AND SMITH, J. E.: *J. Am. Chem. Soc.* **57**, 504 (1935).
- (16) LENHER, S., AND SMITH, J. E.: *Ind. Eng. Chem.* **27**, 20 (1935).
- (17) MCBAIN, M. E. LAING: *J. Am. Chem. Soc.* **55**, 545 (1933).
- (18) MCBAIN, J. W., AND DAWSON, C. R.: *J. Am. Chem. Soc.* **56**, 52 (1934).
- (19) MCBAIN, J. W., DAWSON, C. R., AND BARKER, H. A.: *J. Am. Chem. Soc.* **56**, 1021 (1934).
- (20) MCBAIN, J. W., AND LIU, T. H.: *J. Am. Chem. Soc.* **53**, 59 (1931).
- (21) MORTON, T. H.: *Trans. Faraday Soc.* **31**, 262 (1935).
- (22) NEALE, S. M., AND PATEL, A. M.: *Trans. Faraday Soc.* **30**, 905 (1934).
- (23) NEALE, S. M., AND STRINGFELLOW, W. A.: *Trans. Faraday Soc.* **29**, 1167 (1933).
- (24) NISTLER, A.: *Kolloid-Beihefte* **31**, 1 (1930).
- (25) NORTHROP, J. H., AND ANSON, M. L.: *J. Gen. Physiol.* **12**, 543 (1929).
- (26) OSTWALD, W.: *Trans. Faraday Soc.* **29**, 347 (1933).
- (27) ROBINSON, C.: *Proc. Roy. Soc. London* **148A**, 681 (1935).
- (28) ROBINSON, C.: *Trans. Faraday Soc.* **31**, 245 (1935).

- (29) ROBINSON, C., AND MILLS, H. A. T.: *Proc. Roy. Soc. London* **131A**, 576, 596 (1931).
- (30) ROBINSON, C., AND MOILLIET, J. L.: *Proc. Roy. Soc. London* **143A**, 630 (1934).
- (31) ROSE, R. E.: *Am. Dyestuff Repr.* **21**, 52 (1932); **24**, 97 (1935).
- (32) ROSE, R. E.: U. S. patent 1,674,128, June 19, 1928.
- (33) ROSE, R. E.: *Ind. Eng. Chem.* **25**, 1028 (1933).
- (34) RUGGLI, P., AND FISCHLI, A.: *Helv. Chim. Acta* **7**, 1013 (1924).
- (35) RUGGLI, P., AND PESTALOZZI, S. M.: *Helv. Chim. Acta* **9**, 364 (1926).
- (36) SCHÄFFER, A.: *Z. angew. Chem.* **46**, 618 (1933).
- (37) SCHRAMMEK, W., AND GÖTTE, E.: *Kolloid-Beihfte* **34**, 318 (1932).
- (38) SVEDBERG, T.: *Kolloid-Z.* **36**, *Ergänzungsband*, p. 62 (1925).
- (39) TISELIUS, A.: *Z. physik. Chem.* **124**, 449 (1926).
- (40) VALKÓ, E.: *Trans. Faraday Soc.* **31**, 230 (1935).

CATALYSIS OF IONIC OXIDATION-REDUCTION REACTIONS BY DYES AND ITS PROBABLE MECHANISM¹

P. A. SHAFFER

*Department of Biological Chemistry, Washington University School of Medicine,
St. Louis, Missouri*

Received June 11, 1936

In order to make clear the significance of the main results to be reported briefly in this paper, and indicated in its title, some introductory explanation is called for.

The basic idea underlying nearly all of present-day theory of chemical kinetics is that only *activated* molecules react, and that the absorption of a critical increment of energy is the process of activation. From this point of view reaction velocity is thought to depend merely upon the proportion of the total molecules having a certain energy content or distribution; little or nothing is said about other properties the reacting molecules must possess. The rôle of catalysts, according to this view, is either to provide a different reaction path for which a lower activation-energy level suffices, or to furnish energy-rich molecules to supply the activation energy. Without venturing to estimate, in general, how successful the theoretical treatment based on these concepts is in predicting specific reaction velocity, it seems to the writer that there is reason to doubt whether the energy concept alone is adequate to account for the velocity of many reactions in solution. Additional concepts of a different sort appear to be necessary.

Because many, perhaps most, ionic reactions in solution are immeasurably rapid it has seemed to some logical to infer that ions in general are in an activated state and require for reaction little or no added energy of activation. In making this generalization it appears to have been overlooked that there are many cases where demonstrably ionic—and demonstrably “active”—substances, thermodynamically capable of substantially complete reaction, fail to react or react very slowly. And so far as I know no basis has been suggested for predicting whether a given ionic reaction will be immeasurably rapid or very slow. That there are cases of very slow reaction between demonstrably “active” ions—and also cases of very rapid reaction involving uncharged molecules—would seem to disprove the idea that the ionic state, without further qualification, represents a

¹ Presented before the Thirteenth Colloid Symposium, held at St. Louis, Missouri, June 11-13, 1936.

kinetically activated state. If this argument is valid, the question arises as to what other factors determine reaction velocity.

Some of the striking cases of slow ionic reactions are found among inorganic oxidation-reduction systems. Survey of a number of these (and comparison with rapid reactions of similar type in which one of the "slow" reactants participates with a different partner) led to the hypothesis that one important factor is the equality or inequality of valence change between oxidant and reductant. One of the most remarkable cases is the failure of reaction even on boiling of ceric sulfate and thalious sulfate, both components of reversible, ionic, electromotively active couples. When separated as half-cells of a battery or with a number of catalysts the reaction is fairly rapid and complete at room temperature (10). Another example: titanous chloride (a powerful reducing agent) and iodine in potassium iodide (a fairly strong oxidant) are toward many other substances very rapidly reacting reagents. Both are also electromotively active toward inert electrodes. It is therefore surprising to find that on mixing these two solutions (both in 1 *M* hydrochloric acid) reaction is quite slow, the half-period with 0.01 *N* concentrations being nearly an hour at room temperature. (A number of similar cases, some much more striking, have been examined.)

According to the equi-valence change principle a probable explanation of the slowness of reaction is that Ti^{3+} can give up one electron but not two, while I_3^- (or I_2) can accept two but not one. This explanation is supported by the fact that in this and other similar slow ionic oxidation reactions various substances have marked catalytic effect which are able to be reduced in two steps by the reductant and thereafter to yield two electrons to the oxidant, or *vice versa*.

Among the substances which exhibit marked catalytic effect on the Ti^{3+} and I^- reaction are various dyes, notably indigosulfonates, pyocyanine, and other phenazines, and to less extent rosindulin, flavins, indophenols, and anthraquinone- and naphthoquinone-sulfonates. Can it be shown that these dyes owe their catalytic effect in this reaction to an ability to accept or yield one as well as two electrons? If so, the hypothesis suggests itself that the same property may explain the marked catalytic effect of dyes in other reactions, notably in oxidations by molecular oxygen, including biological respiration. As a matter of fact it was this last problem, the "activation" or "transport" of O_2 in biological oxidations, which directed our interest to a study of the simpler ionic reactions.²

It was observed some years ago that while a number of inorganic ionic

² The points referred to were discussed in some detail in a paper before the Federation of American Societies for Experimental Biology at Cincinnati, April 12, 1933, and in later addresses before several local sections of the American Chemical Society, but have not so far been published.

oxidation reactions comply fairly well with the equi-valence change rule (that is, that reductants requiring the loss of one electron to pass to a known state of higher oxidation are rapidly oxidized by sufficiently powerful oxidants capable of accepting one electron, but generally not rapidly by oxidants requiring two or more electrons), the components of *organic* reversible oxidation-reduction systems appeared to be exceptions to this rule. In virtually all of the many cases of dyes which had been examined at that time, the oxidant and reductant differed by a *pair* of electrons, and the point was emphasized, notably by W. M. Clark, that the two electrons appeared to be gained or lost together, not separately. Yet the oxidized forms were found to be reduced about equally rapidly by, for example, titanous chloride (yielding one electron) and by stannous chloride (yielding two). Similarly the reduced forms are as rapidly oxidized by ferricyanide or ferric ions as by I_2 (or I_3^-), Hg^{++} , or Ti^{3+} , the last three being regarded as two-electron oxidants. This exceptional behavior of dyes was obviously a serious objection to the equi-valence change idea, and left unexplained the very remarkable catalytic action of the dyes in, for example, the reaction of Ti^{3+} and I_3^- , where the addition of a very small concentration of indigocarmine enormously accelerates the oxidation.

A possible way out of the difficulty was indicated by the discovery independently by Elema and by Michaelis of the two-step oxidation-reduction of the natural pigment pyocyanine, and identification of the intermediate between the fully oxidized and fully reduced forms as a unimolecular free radical, a semiquinone. The property thus established for this pigment (and soon thereafter also for rosindulin by Michaelis) of losing one electron in each of two separate steps (as well as two electrons in one step) is precisely the property needed to account for its reactions with both one- and two-electron oxidants and reductants and for compliance with our hypothesis as to the rôle of pyocyanine in catalysis. In the meantime the theory of the two-step reaction and semiquinone formation was formulated by Michaelis and by Elema (6). Could it be that the same property is possessed by the other organic reversible systems above named, even by those for which it has been looked for and not found? This has proved to be the case with a number of these systems, of such diverse structure that it now seems permissible to predict that the two-step oxidation-reduction with intermediate semiquinone formation may be a rather general property, in varying degrees, with many organic systems.

The first case we studied was that of the indigosulfonates. These had been systematically investigated in 1923 by Sullivan, Cohen, and Clark (11), who found no evidence for the existence of an intermediate form. That an intermediate does nevertheless exist seemed probable from the fact that on cautious or slow reduction of indigocarmine at about pH 12 a cherry-color appears between the blue and the yellow of the fully ox-

dized and fully reduced forms. A careful reinvestigation of the four indigo-sulfonates, in collaboration with Dr. P. W. Preisler and later with Dr. E. S. Hill and Mr. Robert Loeffel, gave data the interpretation of which, according to the principles of W. M. Clark and of Michaelis, proves the existence of well-characterized semiquinones. Only preliminary (5, 7, 9) reports have so far been published. In the meantime the catalytically active natural alloxazine pigments, the flavins, were shown by Stern, Kuhn, Hastings, and Stare to exhibit the two-step property on reduction in acid solutions. (The flavins were found to be catalytic in the Ti^{3+} and I_2^- reaction.)

We next turned to the anthraquinonesulfonates, which have the advantage of fair stability in highly alkaline solution, where Michaelis predicted that anionic semiquinones should appear. The anthraquinonesulfonates had been studied by Conant and coworkers (3), who observed abnormal slopes of potentiometric titration curves, which they interpreted as due to meriquinone formation. Dr. E. S. Hill and I (4) found with several of these quinones clear evidence that semiquinones are formed on reduction. On cautious reduction (or reoxidation) an intermediate reveals itself by a characteristic color, the intensity of which is independent of dilution; the slope of the potential-titration curves increases systematically with rise of pH, the E'_0 values being independent of concentration. Very recently Hill and I have reexamined also several hydroxynaphthaquinones, including phthiocol, a pure sample of which was kindly furnished by Professor R. J. Anderson. The latter substance had been studied by Ball (1), who concluded that there was no evidence for semiquinone formation or two-step oxidation. We find, however, what seems to be conclusive evidence with phthiocol of two-step oxidation-reduction at high pH, with semiquinone formation which reaches a maximum of about one-half of the total. The evidence is based on the criteria developed in Michaelis' theoretical analysis and mentioned above in connection with the anthraquinonesulfonates. Statement of the data and their interpretation will be presented in papers now in preparation.

Finally Michaelis (8) reports data showing that β -naphthaquinone-sulfonate exhibits semiquinone formation. We had also observed the abnormal slopes of titration curves and the existence of a colored intermediate with this quinone.

It is significant for our argument that the naphthaquinones and anthraquinones, as well as indigo, pyocyanine, flavin, and rosindulin are all markedly catalytic in the Ti^{3+} and I_2^- reaction and also in the oxidation of glucose in sodium hydroxide solution by oxygen.

There are of course many dyes capable of reversible oxidation-reduction and having catalytic properties in oxidation reactions, for which the two-step process has not so far been demonstrated. Whether in these cases

also the existence of semiquinones can be proved remains to be seen. But in view of the variety of types of structure in which semiquinones have already been found, it seems not unlikely that this property is rather general among reversible organic oxidation-reduction systems, and the writer is disposed, tentatively, to attribute the catalytic activity of such systems in oxidation reactions to the possibly widespread existence of this property. It should be noted in this connection that there are doubtless other ways in which organic systems may exert catalytic activity,—such as complex formation. Also that substances capable of semiquinone formation are not by any means all equally catalytic in any one reaction. The relative levels of the potentials—of the catalyst with respect to that of the primary reductant and of the primary oxidant—appear to be very important. This point obviously concerns the old unsolved problem of the possible relation between dynamics and kinetics (2).

In conclusion I desire to mention a point concerning the behavior and potential of molecular oxygen, and a suggestion as to the possible rôle of catalysts which promote aqueous oxidations by dissolved oxygen. The calculated potential usually cited for the oxygen electrode is 1.23 volts, a value which corresponds to a very intense oxidant, an intensity which if applied unchecked to biological systems should destroy them. The fact is somehow overlooked that this potential is for the reduction of O_2 to $2H_2O$, i.e., for the acceptance by O_2 of four electrons (and $4H^+$ ions). But if the reductant yields to O_2 only two electrons (and $2H^+$ ions are added) H_2O_2 is formed, and for this reaction the normal potential is only 0.68 volt, which at pH 7 is not very far above the intensity level of methemoglobin, an active natural oxidant. Since hydrogen peroxide is known to be formed in many autooxidations by air or oxygen, it seems probable that oxygen in aqueous solutions (including biological respiration) acts at this lower intensity level. If, however, it could be shown that reversible catalysts exist which are capable of yielding simultaneously four electrons to O_2 , (and subsequently accepting electrons in steps of one or two) the full oxidizing intensity of 1.23 volts might perhaps become available. By anchoring such a catalyst at a strategic point in the cell the large energy yield might conceivably be advantageously disposed of. Such a picture is pure speculation, but it provides a possible mechanistic reason for the known fact that the "oxygen-activating" type of respiratory catalyst is essential for the breathing of cells. I know of no other suggestion as to why this type of catalyst is essential.

REFERENCES

- (1) BALL: *J. Biol. Chem.* **106**, 515 (1934).
- (2) See, for example, BARRON: *J. Biol. Chem.* **97**, 287 (1932).
- (3) CONANT, KAHN, FIESER, AND KURTZ: *J. Am. Chem. Soc.* **44**, 1382 (1922).

- (4) HILL AND SHAFFER: J. Biol. Chem. 114, li (1936).
- (5) LOEFFEL: J. Biol. Chem. 109, lvi (1935).
- (6) See MICHAELIS: Chem. Rev. 16, 243 (1935), for a summary of the subject.
- (7) MICHAELIS: Chem. Rev. 16, 282 (1935).
- (8) MICHAELIS: J. Am. Chem. Soc. 58, 873 (1936).
- (9) PREISLER AND SHAFFER: Abstracts of the Eighty-sixth Meeting of the American Chemical Society, held in Chicago, September, 1933.
- (10) SHAFFER: J. Am. Chem. Soc. 55, 2169 (1933); Science 81, 464 (1935).
- (11) SULLIVAN, COHEN, AND CLARK: U. S. Pub. Health Repts. 38, 1669 (1923).

ADSORPTION ON IONIC LATTICES¹

I. M. KOLTHOFF

School of Chemistry, University of Minnesota, Minneapolis, Minnesota

Received June 11, 1936

Although there is an extensive literature on the subject of adsorption by ionic lattices, our knowledge of the subject is still very limited. The adsorbent properties of ionic precipitates are attributed to residual valence forces of the ions in the surface of the lattice. It should be realized that the residual valence forces of ions located on the edges are greater than the forces of those located on the plane surfaces, and the valence forces of ions located on corners are still greater than those of ions on the edges. Hence the adsorptive power of lattice ions located on corners is greater than that of ions on edges, and, in turn, the adsorptive power of ions on the edges is greater than that of ions on the plane surfaces. We will call the area occupied by ions *not* located on the plane surface, *active surface*. At present no method is available for the determination of the active surface. Knowing the microscopic dimensions of a particle, it is possible to calculate the fraction of the surface occupied by ions on the corners and the edges. However, the true active surface may be much greater than that calculated from the microscopic dimensions, since in the latter case it is tacitly assumed that the surfaces are plane. Actually, most of the surface, as a rule, is not perfectly flat, but rather irregular; it contains submicroscopic pits and humps. Especially when dealing with relatively fresh ionic precipitates, the active surface is much greater than that calculated from microscopic measurements. Upon aging, a perfection of the particles takes place, and finally the active surface will approach the value calculated from the microscopic dimensions.

In a study of the adsorbent properties of ionic precipitates it should be realized that quantitatively, as well as qualitatively, adsorption on the active surface may be different from that on the plane surface. There are many indications that colloidal suspensions owe their stability to potential-determining ions adsorbed on the active surface. Upon aging, the particles become more and more perfect, resulting in a decrease of the active surface and consequently in a decrease of the charge of the particles, and in a decrease of the stability of the sol.

¹ Presented before the Thirteenth Colloid Symposium, held at St. Louis, Missouri, June 11-13, 1936.

Various attempts have been made to derive rules which would permit certain predictions regarding the adsorbability of various ions. Originally it was thought (F. Paneth) that the adsorbability of an ion increases with decreasing solubility of the compound formed between the adsorbed ion and the lattice ion of opposite charge. The study of Beekley and Taylor (2) on the adsorption of silver salts on silver iodide showed that this relation between adsorbability and solubility holds very roughly only, and that numerous exceptions occur. Recently Kolthoff and MacNevin (13) investigated the adsorption of various barium salts on well-aged barium sulfate from a medium of 50 per cent ethanol. The following table

TABLE 1
Solubility and adsorbability
Barium salts in 50 per cent ethanol on barium sulfate

BARIUM SALT	ORDER OF ADSORBABILITY EXPRESSED IN $a \times 10^{40}$	RELATIVE SOLUBILITY IN 50 PER CENT ETHANOL	ORDER OF INCREASING SOLUBILITY
1. Bromate.....	1.80	1	1
2. Formate.....	0.91	81	3
3. Nitrate.....	0.69	33	2
4. Perchlorate.....	0.59	1610	7
5. Chloride.....	0.54	223	4
6. Bromide.....	0.37	848	5
7. Iodide.....	0.35	1477	6
8. Thiocyanate.....	0.26	1663	8

* a in the expression: $\frac{x}{m} = ac^{1/n}$ ($1/n = 0.38$).

shows the order of adsorbability and solubility. It was found that the adsorption isotherm follows the Freundlich expression:

$$\frac{x}{m} = ac^{1/n}$$

$1/n$ being about 0.38 for the various barium salts, and the constant a , given in table 1, being a measure of the adsorbability.

Again it is seen that there is no close parallelism between adsorbability and solubility. Particularly the perchlorate is out of place; it is more strongly adsorbed than barium chloride, bromide, or iodide, although its solubility in 50 per cent ethanol is greater than that of the three halides. The adsorbabilities of the bromide and iodide are practically the same, although the solubility of the iodide is much greater than that of the bromide. Fajans and Erdey-Grúz (7) pointed out that in addition to solubility other factors, such as deformation, size of the adsorbed ions, and dissociability of the adsorption complex formed have to be taken into

account. Moreover, the charge (valence) of the adsorbed ions and the deformability of the lattice ions will play a part. Considering the many factors that influence the adsorbability, it is quite plausible that the so-called Paneth-Fajans-Otto Hahn rule can be only of a highly approximate character. On theoretical grounds it might be expected that there should be a simple relation between the heat of solution of the adsorbed compound and its adsorbability; the latter should increase with decreasing heat of solution. Unfortunately, not enough data on the heats of solution in extremely dilute solutions are available in the literature to test the validity of the above rule.

In making systematic adsorption studies, it is of great importance to distinguish between various kinds of adsorption which may occur. This distinction has been overlooked frequently in the literature. This neglect is the cause of considerable confusion regarding the interpretation of experimental results, as will be shown below. In the following, five different kinds of adsorption will be discussed.

1. Adsorption of a salt having an ion in common with the lattice: adsorption of potential-determining ions

Ionic lattices have a pronounced tendency to adsorb lattice ions from a solution. As a matter of fact, the growth of an ionic crystal is a result of successive additions (adsorption) of lattice ions to (on) the surface of the growing particle.

According to Haber and Beutner (8, 19, 25) the thermodynamic potential E of an ionic precipitate, say of silver iodide is equal to:

$$E = C + \frac{RT}{F} \ln a_{\text{Ag}^+} = C' - \frac{RT}{F} \ln a_{\text{I}^-} \quad (1)$$

in which C and C' are constants and Ag^+ and I^- the "potential-determining ions" (20). The adsorption of potential-determining ions is accompanied by the adsorption of an indifferent ion of opposite electrical charge, the total adsorption giving rise to the formation of the so-called double layer. With constant capacity of the double layer, the amount of I^- or Ag^+ (x) taken up by a given amount of silver iodide is proportional to E . Since E is a linear function of $\ln a_{\text{Ag}^+}$ or $\ln a_{\text{I}^-}$ it is found (1) that

$$\begin{aligned} x &= k_1 + k_2 \log C \\ \Delta x &= k \Delta \log C \end{aligned} \quad (2)$$

in which x is the amount adsorbed and C the concentration (actually the activity) of the potential-determining ion.

It should be noted that according to equation 2, the amount of potential-determining ion adsorbed (x) is a simple logarithmic function of the activity

of the ion in the solution, but that no provision is made for the effect of the indifferent ion which is adsorbed simultaneously. Still, we have seen before that the adsorption of a salt containing a lattice ion is also a function of the nature of the indifferent ion.

The validity of equation 2 has been shown to hold true for one case only, namely, for silver iodide. Lange and Berger (21) determined the adsorption of silver nitrate and potassium iodide on freshly precipitated silver iodide at various temperatures. They found that the adsorption of the potential-determining silver and iodide ions agreed with the expression $\Delta x = k\Delta \log C$. They also concluded that silver ions are more strongly adsorbed than iodide ions at the same equilibrium concentration in the solution. This conclusion was based on the erroneous assumption that neither adsorption of silver ions nor of iodide ions occurs at the potentiometric end point or equivalence potential where $c_{Ag^+} = c_{I^-}$. Verwey and Kruyt (28), working with well-aged electro dialyzed silver iodide sols, found that the adsorption of iodide ions follows the expression $\Delta x = k\Delta \log c$. By extrapolation to the point of zero adsorption, they concluded that the zero point charge or isoelectric point of aged silver iodide is found at a silver-ion concentration of 10^{-6} molar, hence in a solution in which the silver-ion concentration is about 10,000 times greater than the iodide-ion concentration. In a precision study carried out in this laboratory by Kolthoff and Lingane (12), it was found that the isoelectric point of fresh silver iodide is at $pAg = 6.0$ and that the adsorption of silver ions follows the expression $\Delta x = k\Delta \log c$. As a result of the asymmetric location of the isoelectric point the "equivalence potential" ($c_{Ag^+} = c_{I^-}$) does not coincide with the stoichiometric end point. As a matter of fact, it was found that upon mixing silver nitrate with potassium iodide at room temperature, the silver iodide at the equivalence potential contained 0.1 of a per cent of iodide in excess. Expressed in other words, on mixing equivalent amounts of silver and iodide the supernatant liquid contains a slight excess of silver and the precipitate a slight amount of adsorbed iodide. Only at the isoelectric point is the silver iodide free of adsorbed silver or iodide salt. Hence it is impossible to prepare pure, relatively fresh silver iodide in equilibrium with its saturated solution in water ($c_{Ag^+} = c_{I^-}$). The solid consists of pure silver iodide only when the silver-ion concentration in the supernatant liquid is equal to 10^{-6} molar. Upon washing such a precipitate with water an adsorption of iodide ions, supplied by solution of the solid silver iodide, will occur. Upon continued washing the counter ions adsorbed with the iodide ions will be hydrogen ions, supplied by the water.

The amounts of silver and iodide adsorbed by the fresh silver iodide in the above experiments were found to be extremely small, although the fresh silver iodide had an extremely large surface. Apparently the adsorp-

tion of silver and iodide ions takes place on the active surface only. If the silver iodide was prepared by slow precipitation at 95°C. the adsorption of silver and iodide ions was found to be reduced to almost negligible quantities, owing to rapid perfection of the particles with a resultant decrease of the active surface.

Although theoretically not expected, it was found by Kolthoff and MacNevin (13) that the adsorption of barium salts from 50 per cent ethanol on barium sulfate does not follow expression 2, but over a wide range of concentrations the relation $\Delta \log x = k\Delta \log C$. The barium sulfate used was a fine, well-aged product, the average dimension of the particles being 0.14 micron. From aqueous medium the adsorption of the barium salts was so small that it was hardly detectable. From a medium consisting of 50 per cent ethanol a marked adsorption occurred; apparently the energy of desolvation of the adsorbed ions is much less in this medium than in water. It may be mentioned that the possibility of the adsorption of un-ionized salt should not be overlooked. It is planned to make a more extensive study of the medium effect upon the adsorption. It was noted that the barium sulfate, upon shaking with solutions of various barium salts in 50 per cent ethanol, had a pronounced tendency to go into colloidal solution. Hence, one would expect to be dealing with adsorption of potential-determining ions (equation 2). On the other hand, the amounts of barium salts adsorbed were found to be much greater than would correspond to an adsorption on the active surface only. It may be that the adsorption on the active surface is governed by equation 2, whereas the adsorption on the plane surface is determined by the Freundlich adsorption isotherm

$$x = ac^{1/n} \text{ or } \Delta \log x = k\Delta \log C \quad (3)$$

which expression was found to hold in this particular case. It may be mentioned that a marked adsorption of calcium bromate (in the form of $\text{Ca}(\text{OH})(\text{BrO}_3)$ as a result of hydrolytic adsorption) and of potassium bromate was found from a medium of 50 per cent ethanol. In these cases we are dealing with a true salt adsorption in the absence of a potential-determining ion, and there is a possibility that in the above case the adsorption of the barium salts is mainly of the latter type.

In the determination of the adsorption of a salt containing a lattice ion, equivalent amounts of cations and anions are found to be removed from solution. Such an experimental result does not always allow the conclusion that equivalent amounts of potential-determining ions and indifferent ions of opposite charge are actually adsorbed. There is a possibility that an exchange, discussed in the following paragraph, occurs with subsequent precipitation of the excess of lattice ions in solution,

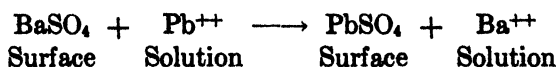
with lattice ions of opposite charge sent into solution, as a result of exchange.

2. Exchange adsorption between lattice ions in the surface and foreign ions from the solution

When an ionic precipitate is in equilibrium with a solution, the speed with which ions leave the surface is equal to the speed with which the ions deposit from the solution on the surface. The equilibrium is kinetic rather than static. One might say that there is a statistical distribution of lattice ions between the surface and the solution. The determination of the specific surface of lead salts with thorium B as radioactive indicator (23, 15) is based upon this principle. Upon shaking a lead salt with a solution containing thorium B; the following relation holds when there is kinetic exchange equilibrium:

$$\frac{(\text{ThB surface})}{(\text{ThB solution})} = \frac{(\text{Pb surface})}{(\text{Pb solution})} \quad (4)$$

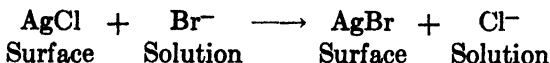
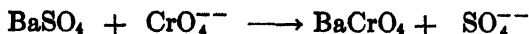
When the solution contains foreign ions which are strongly adsorbed by, and fit into, the lattice a similar exchange may be found between the lattice ions and the foreign ions. For example, upon shaking barium sulfate with lead chloride it was found (22) that lead ions but no chloride ions were removed from solution. Moreover, it was found that for each lead ion removed, a barium ion entered the solution. These experiments show conclusively that the "adsorption" of the lead ions involves an exchange reaction, represented by the equation



Part of the barium ions in the surface are replaced by lead ions. Quantitatively the adsorption is determined by neither equation 2 nor equation 3 (case I) but by an expression similar to equation 4:

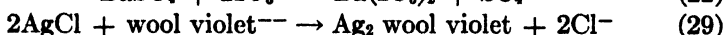
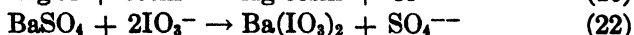
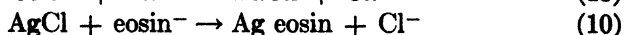
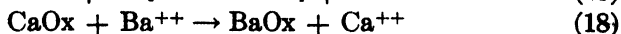
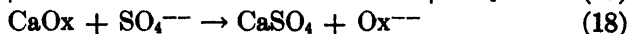
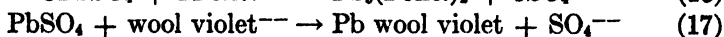
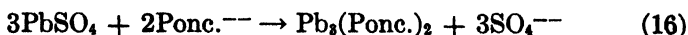
$$\frac{(\text{Pb surface})}{(\text{Pb solution})} = K \frac{(\text{Ba surface})}{(\text{Ba solution})} \quad (5)$$

in which K represents the distribution coefficient of lead between solution and the surface of barium sulfate. The value of K has been determined by Kolthoff and MacNevin (14) by working with barium sulfate of known surface; it was found to decrease with increasing mole percentage of lead in the surface of lead sulfate. A similar exchange occurs in the following cases:



In all these cases the foreign ion fits in the lattice of the adsorbent, and its size is of the same magnitude as that of the replaced ion.

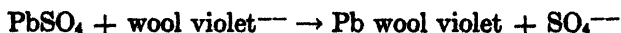
It was found in this laboratory that an exchange of the above nature is not limited by the similarity in size of the exchanging ion and the exchanged lattice ion. As a matter of fact, it is even not necessary that both ions carry the same charge. Below are given some examples of exchange reactions that have been studied, thus showing the general occurrence of the phenomenon; in each case the literature reference follows the equation.



In none of these cases is an equivalent adsorption of cation and anion found, the exchanging ion being removed only, whereas an equivalent amount of exchanged lattice ion is sent into solution. It is possible to interpret the experimental results by a mechanism different from an exchange, although it should be stated that the other interpretations are not very plausible in the cases referred to. More work should be done in order to decide whether all the exchange reactions occurring can be interpreted by the same mechanism. Let us take as an example the adsorption of wool violet on lead sulfate (17). On shaking lead sulfate with the sodium salt of wool violet it was shown experimentally that the dye ion is removed from solution, no sodium ion being adsorbed, and that for each adsorbed wool violet ion a sulfate ion is sent into the solution. The experimental results were interpreted by an exchange mechanism. However, another possible explanation is that the wool violet is adsorbed as lead salt on the surface of lead sulfate, the lead ions being furnished by the saturated solution of lead sulfate. As a result of the disappearance of lead ions, the solution is no longer saturated with the solid, and more lead sulfate will go into solution until equilibrium is restored. The final result then is that equivalent amounts of lead and wool violet ions leave the solution and the latter, therefore, must contain sulfate ions in excess. Verwey (26) has proposed a mechanism different from exchange and from the adsorption of the lead salt of wool violet. According to his interpretation there is a possibility

of the formation of a triple layer, the dye ions being truly adsorbed on the surface. Since the thermodynamic potential of the precipitate is hardly changed by the adsorption, some lead ions are adsorbed in the surface, but most of the lead ions are adsorbed as counter ions. If this interpretation is correct it should be possible to replace the lead ions adsorbed as counter ions by any other cation. Such experiments have not yet been made.

At this point we should add a few words to what has been said in the previous section (case I) on the mechanism of the adsorption of a salt having an ion in common with the lattice. If the ion of the salt foreign to the lattice gives a marked exchange with the lattice ion of the same electrical sign in the surface, we cannot conclude from the experimental results that an equivalent adsorption of lattice ion and foreign ion has occurred. It is true that equivalent amounts of lattice ion and foreign ion are removed from solution, but the foreign ion may disappear as a result of exchange and the lattice ion by precipitation in the form of the adsorbent itself. Let us consider as an example the adsorption of the lead salt of wool violet on lead sulfate. The primary reaction is the following exchange:



The sulfate ions entering the solution as a result of exchange are precipitated as lead sulfate by the excess of lead ions in the solution

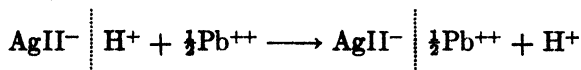


From the analytical results one might conclude that the lead salt of wool violet is adsorbed; actually, however, the wool violet is removed by exchange and the lead ions by precipitation. In experiments carried out by Sandell (18) it was found that iodate ions give an exchange with oxalate ions on the surface of calcium oxalate, but no exchange occurred between iodide and oxalate ions. Even the adsorption of calcium iodide on calcium oxalate was found to be negligibly small, whereas the adsorption of calcium iodate was pronounced. Naturally an excess of calcium ions in the solution favors the exchange between iodate and oxalate ions in the surface of the lattice, as the concentration of the oxalate ions in the solution is decreased by the excess of calcium. Hence, it is quite possible that in this case again we are dealing with an exchange of iodate ions and a subsequent precipitation of calcium oxalate.

3. *Exchange between adsorbed "counter ions" and foreign ions in the solution*

It is well known that colloidal solutions owe their stability in the first place to a primary adsorption of lattice ions, an equivalent amount of foreign ions of opposite sign being adsorbed as counter ions in the mobile part of the diffuse double layer. Exchange between these counter ions

and other ions of the same electrical sign in the solution is determined in the first place by the Schulze-Hardy rule, the exchange ability of an ion increasing strongly with its valence (charge) as shown by Verwey and Kruyt (28) in the case of silver iodide sols. Such an exchange also occurs after the flocculation of the particles, and should be distinguished from true adsorption. Exchange of counter ions does not result in an equivalent adsorption of foreign cation and anion from the solution, but in a removal of the exchanging ion, the latter being replaced by an equivalent amount of the counter ion originally present on the surface. Silver iodide, for example, even after a thorough washing process, contains adsorbed iodide ions and an equivalent amount of hydrogen ions as counter ions. If such a precipitate is shaken, say, with a dilute lead nitrate solution, no nitrate ions are adsorbed, but lead ions exchange with hydrogen ions:



The quantitative relation between amount adsorbed and concentration is quite different from those discussed in the previous paragraphs. For two equally charged ions, for example H^+ and K^+ , Verwey (27) derived that exchange equilibrium² is determined by the expression:

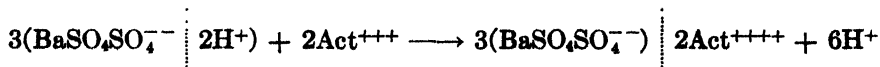
$$\left(\frac{\text{H}^+}{\text{K}^+} \right)_{\text{surface}} = K \left(\frac{\text{H}^+}{\text{K}^+} \right)_{\text{solution}} \quad (6)$$

Apparently activities instead of concentrations should be written in the above expression. However, as long as we are dealing with two ions of the same electrical charge, the concentration relation may be expected to hold within a wide range of ionic strengths. When the two ions differ in charge, the expression may be expected to become extremely complicated. With the aid of the Debye-Hückel expression, the activity coefficients of the two ions in the solution can be calculated approximately with a reasonable accuracy, but nothing is known of the activity coefficients in the double layer. It well may be expected that the activity coefficient of the ions in the double layer will be a function of the thickness of the latter. This thickness depends on the kind and particularly on the valence of the counter ions, thus making a theoretical solution of the problem still more complicated. Numerous studies on the quantitative relationships in exchange reactions on zeolites and soils have been described in the literature, but the significance of activities has not been considered. It should be added that even in the simple case represented by equation 6 it is doubtful whether the value of K may be considered to be constant, when

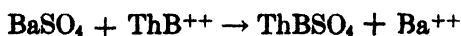
² See, however, the statistical treatment by Jenny (*J. Phys. Chem.* **40**, 501 (1936)), which is quite different.

the surface contains centra of varying activities. Especially when dealing with exchanging ions of different charge, K may be expected to be a function of the activity of the surface. Summarizing then, it may be stated that our knowledge of the quantitative relationships of the exchange of counter ions is still very limited and that more systematic work is desirable.

A distinction between exchange of counter ions and other types of adsorption becomes of primary importance in studies on the adsorption of radioactive ions, in which the amounts of adsorbates used are extremely small. In comparing the kinetics of the adsorption of different radioactive ions, one has to ascertain in the first place whether one is dealing with the same kind of adsorption. This has been overlooked by Imre (9), who compared the adsorption of actinium (a lanthanum homolog) and of thorium B (a lead isotope) on barium sulfate. In the former case he undoubtedly was dealing with an exchange of counter ions:



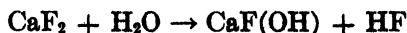
in the latter case also with an exchange between thorium B and barium ions in the surface of barium sulfate.



For this reason the time-adsorption curves of these two ions are not comparable.

4. *Molecular adsorption of non-electrolytes and true adsorption of salts*

Pure precipitates with ionic lattices attract and adsorb water from the atmosphere; this adsorption of water increases with increasing surface development of the precipitate. The adsorbed water can be held very tenaciously. deBoer and Dippel (3) were unable to remove adsorbed water from calcium fluoride at room temperature in a high vacuum. Even upon heating, the adsorbed water was not given off; at 400°C. the water layer could be removed, not by desorption but as a result of a chemical reaction:



Miss deBroeckère (5) found that water adsorbed on barium sulfate was not removed after heating to 250°C., but that at temperatures between 250° and 300°C. it was desorbed quantitatively. Moreover, she claims that the water may be adsorbed in a monomolecular layer. Qualitatively as well as quantitatively, results obtained in this laboratory differ from those of deBroeckère; a final discussion of the matter will be postponed until

more conclusive information has been obtained. Not only water, but also other substances with a dipole character can be adsorbed in a molecular form. We found, for example, that water-free precipitates may adsorb considerable amounts of methanol. In the Harkins' method for the determination of the specific surface with higher fatty acids, use is made of the fact that on the saturated surface these acids form a monomolecular layer, the orientation of the adsorbed molecules and their diameter on the surface being known.

Considering the strong electrical field around the cations and anions in the surface of the lattice, it may be expected that not only dipoles may be adsorbed, but ions as well. Thus, on shaking of an ionic precipitate with a solution of a salt having no ion in common with the lattice, an equivalent adsorption of cations and anions may be anticipated. Actually it is claimed by deBroeckère (6, 24) that various chlorides, bromides, and iodides are adsorbed on the saturated surface of barium sulfate as a monomolecular layer, and that the relation between adsorption and concentration is quantitatively expressed by equation 3. From dilute aqueous chloride solutions there is mainly an adsorption of water molecules, the latter being gradually replaced by the metal chloride with increasing concentration of the latter in the solution. We (11) have not been able to duplicate deBroeckère's experiments, and a final discussion must be postponed until later.³

Recently it has been found in this laboratory (13) that the adsorption of salts depends greatly upon the nature of the solvent. For example, we found that the adsorption of potassium and calcium bromate on barium sulfate was negligibly small from dilute aqueous solutions, whereas a pronounced adsorption occurred from solutions of 50 per cent ethanol. The potassium bromate gave an equivalent adsorption of cations and anions, but in the case of calcium bromate, a hydrolytic adsorption as $\text{Ca}(\text{OH})\text{BrO}_3$ occurred. We plan to study this medium effect in greater detail.

5. Activated adsorption

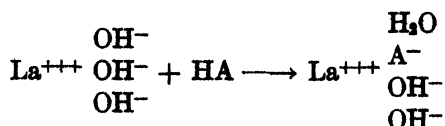
In the preceding section we have seen that non-electrolytes and very weak electrolytes may be molecularly adsorbed on the surface of ionic precipitates. If the adsorbate is a weak acid and the adsorbent a base (hydrous oxides) two different kinds of adsorption may occur:

a. Molecular adsorption. This type of adsorption, for example, occurs upon shaking a suspension of hydrous aluminum oxide with dilute solutions

³ Miss de Broeckère and the author will exchange samples of barium sulfate, in order to decide whether the discrepancy can be attributed to a great difference in specific surface of the products with which the work was performed.

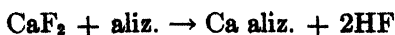
of phenolphthalein or thymolphthalein, in which case the undissociated acid molecules are adsorbed.

b. Activated adsorption. If the adsorption energy is great enough to overcome the dissociation energy of the adsorbate, the latter will be adsorbed in the ionized form. This case occurs, for example, upon shaking a suspension of lanthanum hydroxide with thymolphthalein:



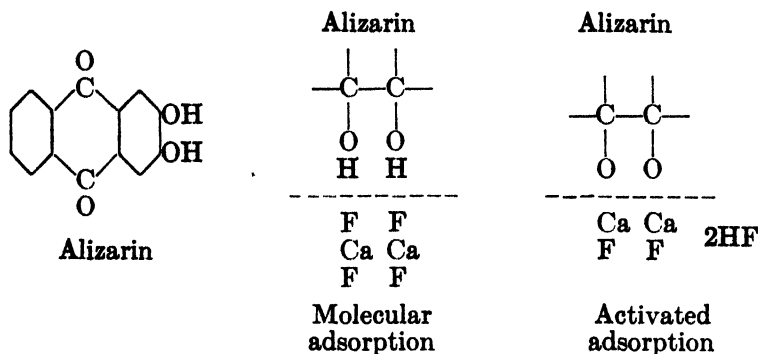
Lanthanum hydroxide is a strong, but only slightly soluble base, its saturated solution in water having a pH of about 9. At this pH thymolphthalein is still present in the colorless form. When a suspension of the base is shaken with the indicator the color turns to a beautiful blue. After settling, the supernatant liquid is colorless; but the precipitate, containing the adsorbed indicator in the ionized form, is strongly colored. This distinction between molecular and activated adsorption may permit us to draw definite conclusions regarding the basicity of the hydrous oxides in the solid state.

Dependent upon the experimental conditions, a substance may be adsorbed in the molecular or activated form. Reference is made to the beautiful investigations of deBoer (4) and coworkers on the adsorption of alizarin and other compounds from the gaseous phase on thin sublimed layers of calcium, barium, and strontium fluorides and barium chloride. At temperatures below 300°C. a molecular adsorption of alizarin on calcium fluoride occurs. The adsorbed dye has a red-brown color and can be extracted completely with amyl alcohol. When the temperature is increased to 400°C. the color of the adsorbed alizarin changes from a red-brown to a brick-red. The dye is now adsorbed in the activated state



and cannot be removed from the surface by extraction with amyl alcohol. Treatment with hydrochloric acid is necessary in order to decompose the adsorption compound. In this case of activated adsorption the fluoride ion in the calcium fluoride functions as the base similar to the hydroxyl ion in the lanthanum hydroxide.

Schematically the two kinds of adsorption may be represented in the following way:



In this case the type of adsorption is determined primarily by the dissociation energies of the adsorbed acid and of hydrofluoric acid. If the adsorbate is a relatively strong acid, its proton can be captured by the fluoride ion at low temperatures and an activated adsorption will be found. This case occurs with picric acid. If, on the other hand, the adsorbate is an extremely weak acid, such as *p*-nitrophenol, a molecular adsorption will result only, as the dissociation energy of the adsorbed acid is much greater than that of the hydrofluoric acid. The case of alizarin is intermediate between these two: at lower temperatures (300°C.) its dissociation energy is greater than that of hydrofluoric acid (we neglect polarization of the alizarinate or fluoride ion), at higher temperatures the reverse is true.

Comparable to this case is the adsorption of water on calcium fluoride. We have seen that at low temperatures the water is adsorbed in the molecular form, but that at 400°C. an activated adsorption occurs with the evolution of an equivalent of hydrogen fluoride.

SUMMARY

In systematic studies of the adsorbent properties of ionic precipitates distinction has to be made between different types of adsorption. These various types are discussed from a qualitative and quantitative viewpoint.

REFERENCES

- (1) ANDAUER, M., AND LANGE, E.: Z. physik. Chem. **156A**, 241 (1931).
- (2) BEEKLEY, J. S., AND TAYLOR, H. S.: J. Phys. Chem. **29**, 942 (1925).
- (3) DE BOER, J. H., AND DIPPEL, C. J.: Z. physik. Chem. **25B**, 399 (1934).
- (4) DE BOER, J. H.: Z. physik. Chem. **13B**, 134; **14B**, 149, 457 (1931); **15B**, 300; **16B**, 397; **17B**, 161 (1932).
- (5) DE BROECKÈRE, L.: Bull. soc. chim. Belg. **41**, 410 (1932).
- (6) DE BROECKÈRE, L.: J. chim. phys. **26**, 250 (1929); **27**, 543 (1930); Bull. acad. roy. Belg. **17**, 1249 (1931); Bull. soc. chim. Belg. **38**, 409 (1929); **41**, 40 (1932); Compt. rend. **198**, 822 (1934).
- (7) FAJANS, K., AND ERDEY-GRÚZ, T.: Z. physik. Chem. **156A**, 97 (1931).
- (8) HABER, F., AND BEUTNER, R.: Ann. Physik [4] **26**, 947 (1908).

- (9) IMRE, L.: Z. physik. Chem. **164A**, 327 (1933); Z. Elektrochem. **38**, 535 (1932).
- (10) KOLTHOFF, I. M.: Kolloid-Z. **68**, 190 (1934).
- (11) KOLTHOFF, I. M.: Chem. Weekblad **33**, 321 (1936).
- (12) KOLTHOFF, I. M., AND LINGANE, J. J.: J. Am. Chem. Soc. **58**, 1528 (1936).
- (13) KOLTHOFF, I. M., AND MACNEVIN, WM. M.: J. Am. Chem. Soc. **58**, 1543 (1936).
- (14) KOLTHOFF, I. M., AND MACNEVIN, WM. M.: J. Am. Chem. Soc. **58**, 725 (1936).
- (15) KOLTHOFF, I. M., AND ROSENBLUM, CH.: J. Am. Chem. Soc. **55**, 2656 (1933).
- (16) KOLTHOFF, I. M., AND ROSENBLUM, CH.: J. Am. Chem. Soc. **55**, 2664 (1933).
- (17) KOLTHOFF, I. M., VON FISCHER, W., AND ROSENBLUM, CH.: J. Am. Chem. Soc. **56**, 834 (1934).
- (18) KOLTHOFF, I. M., AND SANDELL, E. B.: J. Am. Chem. Soc. **55**, 2170 (1933).
- (19) VAN LAAR, J. J.: Lehrbuch der Theoretischen Elektrochemie (1907).
- (20) LANGE, E., AND BERGER, R.: Z. Elektrochem. **36**, 171 (1930).
- (21) LANGE, E., AND BERGER, R.: Z. Elektrochem. **36**, 980 (1930).
- (22) NOPONEN, G.: Thesis, University of Minnesota, 1936.
- (23) PANETH, F.: Physik. Z. **15**, 924 (1915).
PANETH, F., AND VORWERK, W.: Z. physik. Chem. **101**, 445 (1922).
- (24) PINKUS, A., AND DE BROECKÈRE, L.: J. chim. phys. **25**, 605 (1928).
- (25) VERWEY, E. J. W.: Chem. Rev. **16**, 363 (1935).
- (26) VERWEY, E. J. W.: Kolloid-Z. **72**, 187 (1935).
- (27) VERWEY, E. J. W.: Chem. Weekblad **31**, 789 (1934).
- (28) VERWEY, E. J. W., AND KRUYT, H. R.: Z. physik. Chem. **167A**, 149 (1933).
- (29) YUTZY, H.: Thesis, University of Minnesota, 1936.

THE GELATION OF BENTONITE SUSPENSIONS¹

GOEFFREY BROUGHTON² AND LOMBARD SQUIRES

*Department of Chemical Engineering, Massachusetts Institute of Technology,
Cambridge, Massachusetts*

Received June 11, 1936

It has been known for some years that certain sols, on standing, form gels which can be reliquefied by shaking. This phenomenon was first discovered by Schalek and Szegvary (13) in 1923 for ferric oxide sols to which a small amount of electrolyte, for example, sodium chloride, had been added. Since then many cases of this isothermal reversible sol-gel transformation, which Freundlich has termed "thixotropy," have been reported.

Bentonite, a clay-like material, probably of volcanic origin and found largely in Wyoming, exhibits thixotropy to a marked degree in aqueous suspensions. Suspensions of suitable concentration will set to a gel in a few seconds, although a number of other factors materially influence this setting time. Particle size undoubtedly plays a great part, since centrifuged suspensions will give dispersions showing thixotropy down to at least a concentration of 1 per cent, whereas ordinary bentonite suspensions require a concentration of over 4 per cent.³ The hydrogen-ion concentration of the suspension, as might be expected, was also found by Freundlich, Schmidt, and Lindau (5) to be of great importance. Acid-washed bentonite or electrodialed bentonite suspensions do not show thixotropic behavior. In this paper the effects of temperature and concentration upon gelation are described. No attempt has been made to determine the influence of pH, the hydrogen-ion concentration being kept as constant as possible.

METHODS OF MEASUREMENT

The investigation of thixotropy is greatly hampered by the lack of an adequate method of measurement. The inverted-tube method first introduced by Schalek and Szegvary (14) has been most commonly used. The sol is introduced into a tube, which is stoppered or preferably sealed

¹ Presented before the Thirteenth Colloid Symposium, held at St. Louis, Missouri, June 11-13, 1936.

² Fellow of the Salters' Institute of Industrial Chemistry, London, England.

³ Centrifuged dispersions will be termed "ultrabentonite" in the following in order to distinguish them from ordinary bentonite suspensions.

off. After vigorous shaking the tube is allowed to stand undisturbed in a vertical position for a known time and then inverted. If flow occurs down the wall of the tube, the sol is said to be still liquid. If no flow is apparent then the sol is said to have solidified. By trial and error a time interval can be found below which flow occurs and above which there is no flow. This is called the setting time; its reciprocal is taken as the rate of gelation.

TABLE 1

The effect of the amount of material upon the time of setting
 Ultrabentonite, 2.09 per cent; pH, 7.84; T , 27.5°C.

TUBE DIAMETER	AMOUNT OF LIQUID	SETTING TIME
mm.	cc.	seconds
7.5	1	405
	1.5	395
	2.0	405
9.6	1.0	1485
	2.0	1485

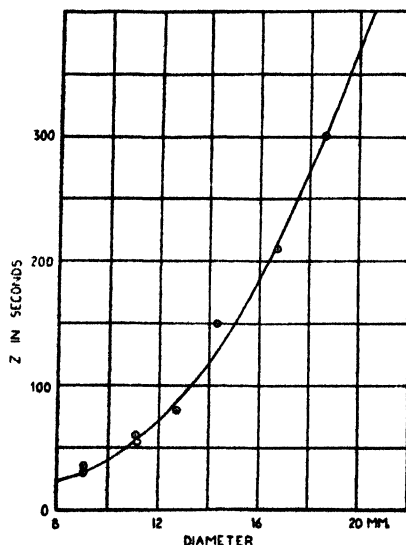


FIG. 1. Effect of diameter of tube upon time of setting of ultrabentonite at 27.5°C.

Theoretically, it is seen that this setting time must depend upon a number of factors,—the strength of the gel formed; its weight, the surface tension of the suspension, etc. Practically, it varies greatly with the diameter of the tube; also great care has to be taken in inverting the tube, since slight shaking may cause flow to occur when none would take place

with gentle inversion. With care consistent results can be obtained, although these vary with the observer. One would desire a true history of the development of gel structure, i.e., of resistance to initiation of flow, but the inverted-tube method unfortunately only gives one point upon such a curve.⁴

In spite of the extensive use of the inverted-tube method, little appears to have been published upon the influence of amount of material enclosed in the tube, the diameter of the tube, etc. As is evident from table 1, within reasonable limits the former has no effect upon the setting time.

On the other hand, the diameter of the tube has a very marked effect,

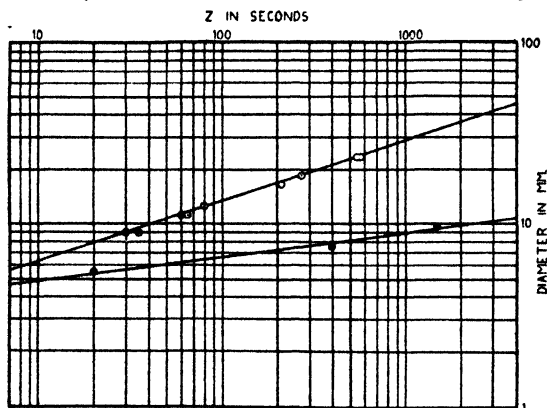


FIG. 2. Effect of diameter of tube upon setting time at 27.5°C. ○, 6.60 per cent bentonite; □, 2.09 per cent ultrabentonite.

as seen from figure 1. Approximately, at least, the relation between tube diameter and setting time for a given suspension and temperature is

$$z = kD^n \quad (1)$$

where z is the setting time, D the internal diameter of the tube, and k and n are constants. Figure 2 shows that the diameter of the tube has a greater influence upon ultrabentonite than upon the crude suspensions. Its influence also decreases with temperature.

The values of k and n unfortunately vary according to the suspension examined, so that no general correction factor can be given for changing tube diameter (table 2). Furthermore, as will be shown later, the temperature coefficient of the setting time of a given suspension is not independent of the tube in which it is measured.

⁴ As Freundlich and Rawitzger (4) have stated, "The setting time is characterized neither through a certain variation of tensile strength nor through an abrupt variation in the velocity of transition. In no respect does it represent a unique point on the solidification curve. For comparison of different sols the setting time is nevertheless very suitable."

These considerations led to the view that another method of measuring the rate of gelation of thixotropic suspensions would be desirable. Freundlich and Rawitzer (4) measured the tensile strength of a ferric oxide sol by means of a cup suspended by a torsion wire in the sol contained in an outer cylinder, which could be rotated. Pryce-Jones (12) adopted a similar but more elaborate device. Such methods, while useful in showing

TABLE 2
Values of k and n for different suspensions

TEMPERATURE	SUSPENSION	CONCENTRATION	k	n
°C.		per cent		
27.5	Bentonite	6.60	0.044	3.0
27.5	Ultrabentonite	2.09	0.000038	7.8
75.0	Ultrabentonite	2.09	1.8	2.1

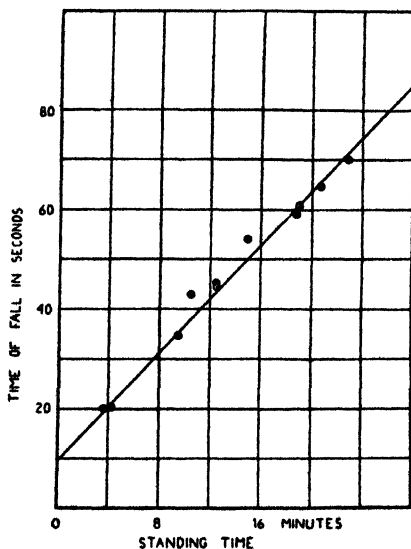


FIG. 3

FIG. 3. Effect of diameter of viscometer upon time of setting. \circ , viscometer I, internal diameter 1.2 cm.; \otimes , viscometer II, internal diameter 1.5 cm.

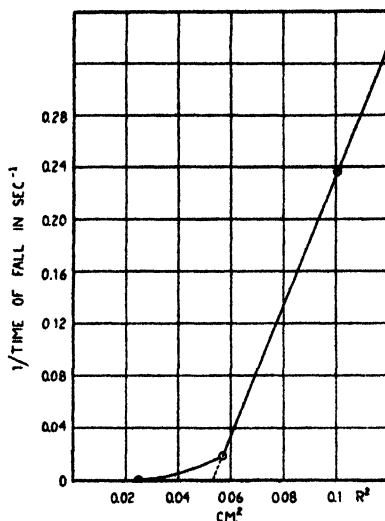


FIG. 4

FIG. 4. Ultrabentonite at 55°C. Standing time, two hours. Velocity of sphere plotted against the square of its radius.

there is no abrupt transition between sol and gel, require elaborate apparatus and care in operation while still yielding only comparative results. A more natural property to investigate appears to be the viscosity of the sol. In fact, most studies of the gelation of emulsoidal solutions have been made by viscosity measurements. Gelation is a kinetic process, almost certainly consisting of the building-up of a structure, which inter-

feres with the flow of the liquid. Unfortunately most methods of measuring viscosity cause simultaneously the breakdown of this gel structure to an unknown degree. The falling-ball viscometer has, however, the advantage that the sphere continuously passes on to the undisturbed suspension, so that its travel is relatively free from the effects of structure breakdown. This led to a decision to use the falling-ball method in measuring the rate of gelation of bentonite suspensions.

The ordinary type of falling-ball viscometer was used (1). The tube had a width of about 12.5 mm., and a glass tap was fused to the lower end to facilitate the removal of the dropped balls. The distance between marks was 13.9 cm. The viscometer was placed in a thermostat, the temperature of which could be kept constant to $\pm 0.25^\circ\text{C}$. Glass balls about 5 mm. in diameter were first used, since Freundlich (2) has pointed out that the pH, and as a consequence the setting time, of ferric oxide sols is altered by contact with metal. Steel balls about $\frac{1}{16}$ in. in diameter were afterwards used, but no irregularities in behavior were observed. The sol was placed in the viscometer, allowed to come to the temperature of the bath, shaken well, and replaced. After the sol had stood for a known length of time the ball was dropped and the time of fall taken. In this way a curve such as that shown in figure 3 could be obtained.

No attempt was made to convert the times of fall into absolute viscosities, for several reasons. Ultrabentonite belongs to the class of substances showing plastic flow. That is, it possesses a definite yield point and its apparent viscosity is not independent of the shearing force. For a true liquid the curve connecting velocity and the square of the radius of the sphere would be a straight line passing through the origin. This is not the case for ultrabentonite (figure 4). Furthermore, Stokes' law, upon which any calculations would have to be based, is derived for the case of a homogeneous fluid and cannot hold for a gelling sol. Nevertheless, measurements using the same sphere and viscometer give comparative results for the rates of gelation over the whole curve, and not merely for one particular point.

Time of fall is linear in standing time, at least during the early stages of gelation and

$$y = ax + b \quad (2)$$

where y is the time of fall, x the time of standing, and a and b are constants. Granting that the degree of development of structure, i.e., gelation, is proportional to the increase in time of fall, it follows that the rate of gelation, as measured with a given ball, is independent of the time of standing. This surprising result shows a marked difference from the case of emulsoidal gel formation. Thus Mardles (10), for cellulose acetate gels in benzyl alcohol and other solvents, found by the falling-ball method that

$$\eta - \eta_0 = ae^{kt} \quad (3)$$

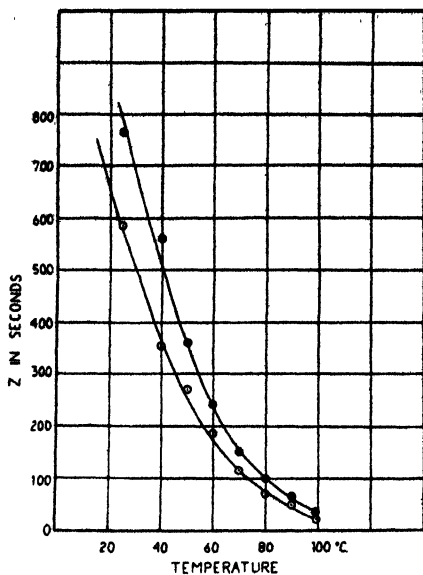


FIG. 5

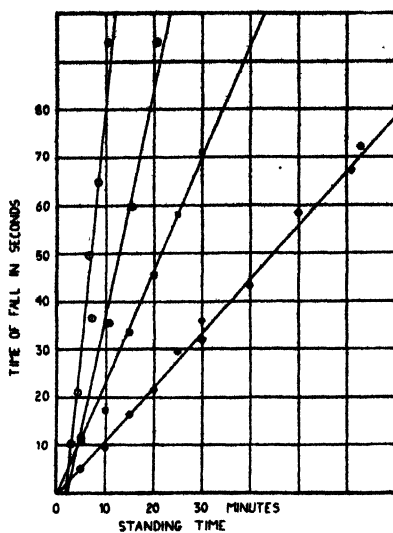


FIG. 6

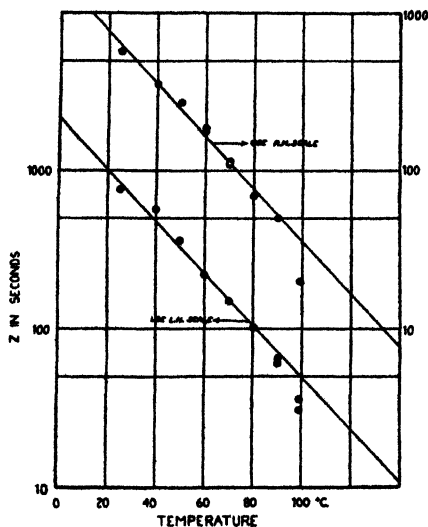


FIG. 7

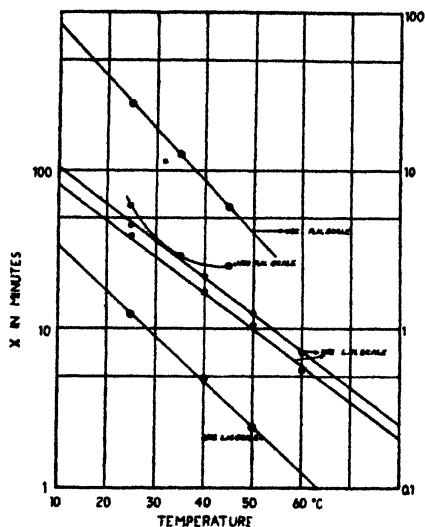


FIG. 8

Fig. 5. Effect of temperature on setting time. \otimes , 2.09 per cent ultrabentonite; \circ , 2.19 per cent ultrabentonite.

Fig. 6. Effect of temperature upon setting time of 2.09 per cent ultrabentonite. \diamond , 25°C.; \square , 40°C.; \otimes , 50°C.; \circ , 60°C.

Fig. 7. Effect of temperature upon setting time. \otimes , 2.09 per cent ultrabentonite; \circ , 2.19 per cent ultrabentonite. Diameter of tube, 9.6 mm.

Fig. 8. Effect of temperature on standing time (x). Time of fall = 50 secs. \diamond , 2.09 per cent ultrabentonite; \square , 2.19 per cent ultrabentonite; \otimes , 2.55 per cent ultrabentonite; \circ , ultrabentonite and 15 per cent ethyl alcohol; \boxtimes , ultrabentonite and 0.5 per cent gelatin.

where η is the viscosity at time t , η_0 is the viscosity at zero time, and a and k are constants. These viscosities are proportional to his times of fall, since they were calculated directly from these, ignoring the objections mentioned above.

It will be noticed that the rate of gelation is also independent of the diameter of the viscometer tube.

TABLE 3
Values of A and B for two ultrabentonites differently prepared

CHARACTER OF SUSPENSION	CONCENTRATION	pH	A	B	A'	B'
	per cent					
Centrifuged twice	2.09	7.84	0.0165	3.34	0.021	1.98
Centrifuged once	2.19	8.40	0.0173	3.28	0.022	1.95

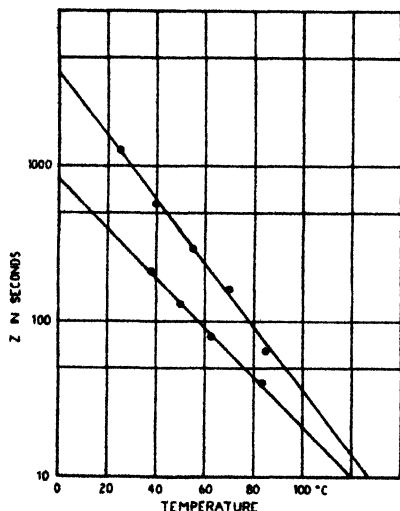


Fig. 9

FIG. 9. Effect of diameter of tube on the temperature coefficient. 2.55 per cent ultrabentonite. \odot , diameter of tube 11.11 mm.; \circ , diameter of tube 12.70 mm.

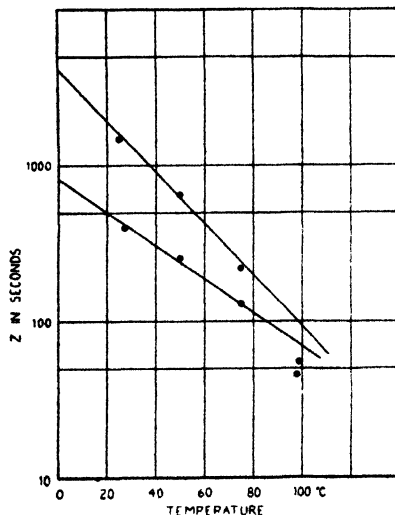


Fig. 10

FIG. 10. Effect of diameter of tube on the temperature coefficient. 2.09 per cent ultrabentonite. \odot , diameter of tube 9.5 mm.; \circ , diameter of tube 7.5 mm.

THE EFFECT OF TEMPERATURE

The effect of temperature upon gelation was examined by both methods. Schalek and Szegevary (14) found for ferric oxide sols that if t is the temperature in $^{\circ}\text{C}$. then

$$\log z = -At + B \quad (4)$$

where A and B are constants and z the setting time. Increase in temperature in bentonite suspensions likewise causes gelation to become much more rapid (figures 5 and 6), and for both methods the results can be expressed by equations of the form of equation 4. In the falling-ball method, if the standing times at various temperatures for a given time of fall are plotted against temperature on semilog paper, a straight line (figure 8) is again obtained or

$$\log x = -A't + B' \quad (5)$$

where x is the standing time and A' and B' are constants. Furthermore, it was found that two ultrabentonites, prepared by different methods and having slightly different compositions, gave the same values of A and

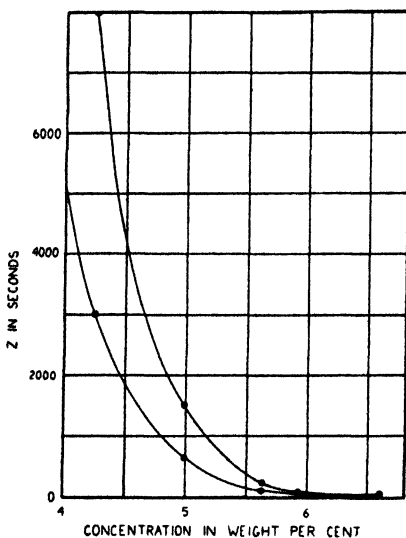


Fig. 11. Effect of concentration on time of setting in a 9-mm. tube. ⊗, 25°C.; ⊙, 55°C.

B in the inverted-tube method, and also gave the same values of A' and B' in the falling-ball method, as shown by table 3.

The constants A and B , however, are changed if tubes of different diameters are used for the same suspension, as shown by figures 9 and 10. This limits their value for comparative use, as, for suspensions of widely differing concentrations, measurements cannot be made in the same tube.

The effect of temperature upon the rate of gelation again presents a distinct difference from the behavior of emulsoid sols. Emulsoid sols, such as that of gelatin, do not gel under any conditions above a certain temperature, whereas bentonite suspensions apparently gel at any temperature. Furthermore, the rate of gelation of gelatin increases on

lowering the temperature (8). In contradistinction to this, bentonite suspensions, as can be seen from figure 6, gel much more slowly at low temperatures.

THE EFFECT OF CONCENTRATION

Concentration has a very great influence upon the setting time of bentonite suspensions. The suspensions referred to in figure 11 were made up by diluting a strong suspension of bentonite and varied slightly in pH from 9.3 to 9.6, the weakest suspension having the highest pH. This change in pH was probably insufficient to affect the setting times materially.

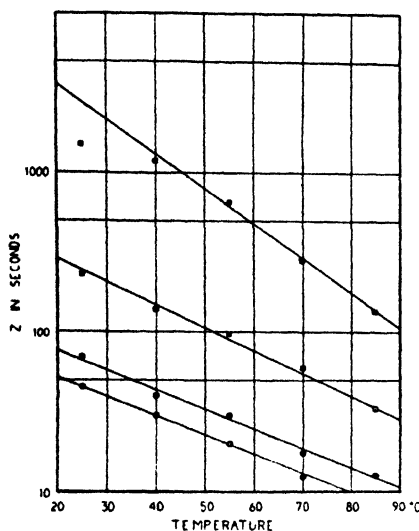


FIG. 12. Effect of concentration on temperature coefficient. Diameter of tube 9 mm. \boxtimes , 4.99 per cent bentonite; \square , 5.63 per cent bentonite; \odot , 5.93 per cent bentonite; \circ , 6.60 per cent bentonite.

Concentration does not affect the temperature coefficient A in equation 4 as greatly as does a change in tube diameter (figure 12).

DISCUSSION

It is seen that the inverted-tube method is capable of giving comparative results providing care in manipulation is exercised and the diameter of the tube in which the measurements are made is kept constant. The falling-ball method is preferable in that it gives the whole of the gelation-time curve and not simply one point. The results of the two methods appear to be in agreement.

The explanation of gelation and thixotropy, as shown by bentonite

suspensions, is difficult. Hauser (6), observing the behavior of very dilute bentonite suspensions under the microscope, found the particles in Brownian motion. Addition of electrolyte caused translation to cease, and still greater quantities of electrolyte caused the cessation of rotary motion. Providing addition of electrolyte had not been too great these changes could be reversed by agitation. Addition of a hydrophilic sol, itself showing Brownian motion, e.g., gum mastic, resulted in cessation of the motion of the gum mastic particles when gelation occurred. There seems no doubt that some sort of structure is built up as the gel forms; the difficulty is to account for gelation at the extremely low concentrations at which it occurs (certainly less than 1 per cent in some cases). For bentonite, two alternative hypotheses have been suggested. The first might be termed the mechanical or "house-of-cards" theory, the clay particles being visualized as flat plates, so packed in three-dimensional, random orientation, edge touching edge in the gel, that movement is impossible

TABLE 4

Effect of a diluent on setting time

2.55 per cent ultrabentonite; 3 cc. used for each experiment

DILUENT ADDED	^s (WATER ADDED)	^s (C ₂ H ₅ OH ADDED)
cc.	seconds	seconds
0	165	165
0.125	420	210
0.25	720	370
0.50	1800	335
0.75		480

and a solid house-of-cards structure is set up (9). The chief objection is that in order to obtain interference between the particles at the low concentrations at which gelation is observed, the particles must be plates, having a length and width much greater than their thickness, the ratio between these quantities being of the order of 100 to 1 or over, which seems extremely great. On the other hand, although direct microscopic evidence is lacking, this theory of the bentonite plates being of microscopic thickness and macroscopic length and width was first put forward by Wherry (15) on microscopic grounds. X-ray evidence has also shown that the bentonite clays are made up of silica and gibbsite (Al₂(OH)₆) layers, which are separated by water (11). The spacing due to this separation varies with the water content of the clay, and thus it appears that in a large excess of water, the layers may actually break away from each other and behave as plates of molecular thickness. Other properties of the bentonites, e.g., adsorptive power, are also in agreement with the thickness of the plates being of molecular or colloidal dimensions.

The only other theory to receive serious consideration has been the suggestion that the clay particles adsorb layers of water sufficiently thick to build up quasi-fluid particles occupying enough volume so that interference is sufficient to induce gelation. This hypothesis requires the formation of water hulls around the particles many molecules thick (which seems unlikely). Bentonite gels have also been shown to possess a tensile strength, which is hard to explain on the basis of particles with adsorbed water surfaces touching each other (9). As a general rule solvation decreases with temperature and one would, therefore, expect the water hulls, if such are formed, to decrease in thickness with increasing temperature, thus leading to a decrease and not an increase in rate of gelation. Further evidence against the water-hull hypothesis is also provided by experiments in which alcohol was added to a bentonite suspension (table 4). The setting time of the suspensions remained nearly constant, whereas addition of water in equal amounts by volume caused the setting times to become indefinitely great. Alcohol is usually considered to act as a dehydrating

TABLE 5
Values of the temperature coefficient

	a_1/a_2
Temperature interval:	
40-50°C.	2.02
40-50°C.. . . .	1 52
40-50°C.... . . .	2 22
Calculated value	1.24
Value from ordinary chemical reaction	2-3

agent when added to aqueous colloids; thus, on the water-hull theory, one would expect it to be even more effective than water in increasing setting time. The viscosity of an alcohol-water mixture is greater than that of either pure component, hence Brownian motion would be retarded and an increase in this factor could not account for the more rapid gelation.

On the other hand, the mechanical theory of gelation seems at first sight equally unable to account for the rapid increase in rate of gelation with temperature, unless further assumptions are made. Freundlich has attempted to draw a parallel between the coagulation of hydrophilic sols and the gelation of thixotropic sols. It is true that the rate of change increases with rise of temperature in each case, but the increases are of a different order of magnitude. According to the von Smoluchowski theory of coagulation the time of coagulation should be proportional to η/T , where η is the viscosity of the solvent and T the absolute temperature. This was experimentally confirmed by Freundlich and Basu (3) for the coagulation of a copper oxide sol by sodium sulfate. Some experimental

values of the temperature coefficient, i.e., the ratio of the rates of change for temperatures 10°C. apart are compared in table 5 with the value which might be expected for aqueous bentonite suspensions. The constants a in equation 2 for the falling-ball method were used.

Evidently, the phenomenon of thixotropy in bentonite suspensions is not truly analogous to coagulation. On the mechanical theory the bentonite particles, even immediately after shaking, are in close juxtaposition, although the strength (and hence the apparent viscosity) of the gel is small. Each subsequent impact between particles builds up the strength as they become more firmly fixed in position, and thus the apparent viscosity increases. However, as the structure becomes stronger, collisions

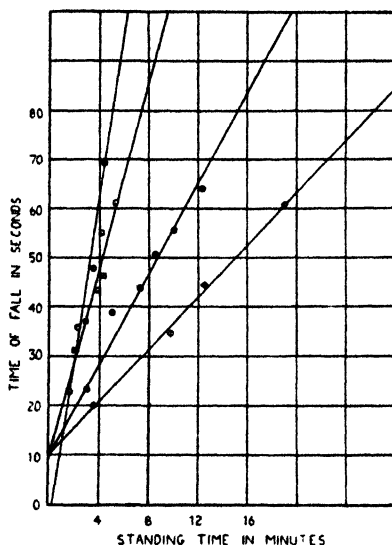


FIG. 13. Effect of addition of 0.5 per cent gelatin. \odot , 25°C. ; \square , 35°C. ; \odot , 45°C. ; \diamond , original sol at 25°C.

of ordinary impact energy have little or no effect, whereas collisions of abnormally great impact energy, of which there will always be some from the distribution theory, have a disproportionate effect in raising the strength. In a coagulation process the particles have a tendency to agglomerate, whereas in the thixotropic gelation of bentonite the particles have a tendency to keep apart and are only forced into contact by continual impacts. After a time, only impacts of exceptional energy are effective in causing increase in gel strength. Temperature causes an increase in these impacts of abnormal energy and hence a quite disproportionate increase in the gel strength. In other words, the gel strength is not proportional to the number of impacts, but depends much more upon their energy content. Hence the influence of temperature is explained by the

great increase in strength brought about by the greater number of high energy impacts.

The action of alcohol is difficult to explain; possibly it affects the ionization of the clay particles or the electrical forces acting between them. Gelatin likewise increases the rate of gelation, as can be seen from figure 13; possibly the adsorbed gelatin on the particles allows a structure to be built up more easily.

The mechanical theory of thixotropy also receives support from the fact that thixotropic sols, as far as has been at present investigated, show no change in their physical properties upon gelation. No work appears to have been done upon bentonite, but Heyman (7) has shown that if there is any volume change in an iron oxide sol upon gelation it is less than 0.0002 per cent. Other evidence, particularly the viscosity characteristics, has also been cited in a previous paper (9).

SUMMARY

Two methods have been developed for measuring the rate of gelation of bentonite suspensions. The first measures the time elapsed after the suspension has been shaken before a tube containing it can be inverted without flow. In the second the velocity of fall of a sphere through the suspension is measured at different times after shaking. Both give results qualitatively in agreement but the latter method is preferred, since it is independent of the diameter of the containing vessel and gives the entire gelation-time curve.

The results are found to be in conflict with the water-hull theory of gel structure and to be qualitatively in agreement with the mechanical theory, in which the gel is pictured as made up with bentonite plates of molecular thickness touching in completely random, three-dimensional orientation.

REFERENCES

- (1) SEC, e.g., BARR: *A Monograph of Viscometry*. Oxford (1931).
- (2) FREUNDLICH: *Thixotropy*. *Actualités Scientifiques et Industrielles*, No. 267. Plermann & Cie, Paris.
- (3) FREUNDLICH AND BASU: *Z. physik. Chem.* **115**, 203 (1925).
- (4) FREUNDLICH AND RAWITZER: *Kolloidchem. Beihefte* **25**, 231 (1927).
- (5) FREUNDLICH, SCHMIDT, AND LINDAU: *Kolloidchem. Beihefte* **36**, 43 (1932).
- (6) HAUSER: *Kolloid-Z.* **48**, 57 (1929).
- (7) HEYMAN: *Trans. Faraday Soc.* **32**, 462 (1936).
- (8) LAMPITT AND MONEY: *J. Soc. Chem. Ind.* **55**, 88T (1936).
- (9) LEWIS, SQUIRES, AND THOMPSON: *Trans. Am. Inst. Mining Met. Engrs.* **118**, 1 (1936).
- (10) MARDLES: *Trans. Faraday Soc.* **18**, 327 (1923).
- (11) MARSHALL: *Science Progress* **30**, 422 (1936).
- (12) PRYCE-JONES: *J. Oil Colour Chem. Assoc.* **17**, 305 (1934).
- (13) SCHALEK AND SZEGVARY: *Kolloid-Z.* **32**, 318 (1923).
- (14) SCHALEK AND SZEGVARY: *Kolloid-Z.* **33**, 326 (1923).
- (15) WHERRY: *Am. Mineral.* **10**, 120 (1925).

THE ADSORPTION OF COMPLEX AMMONIO IONS BY SILICA GEL¹

L. H. REYERSON AND R. E. CLARK

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota

Received June 11, 1936

The discovery that the complex ammonio ions of copper and nickel were strongly adsorbed by silica gel was previously reported by Smith and Reyerson (4). These authors used the adsorption of these complex ions to prepare silica gels containing finely divided metals on the surfaces of the gel by reducing these adsorbed ions at higher temperatures with hydrogen. It was found in the course of these studies that the adsorption forces were so strong that the silica gel containing the complex ammonio ions of copper could be shaken with distilled water for long periods of time, and yet the most sensitive chemical tests were unable to detect any traces of copper ion in the water, which remained colorless. Dr. M. G. Larian of this laboratory reported to the authors that 10 gallons of distilled water, to which ammonia had been added, contained sufficient traces of copper to induce a slight blue coloration in silica gel which was shaken with the water.

Ordinary electrodialysis failed to remove the adsorbed ions to any extent, but changes took place after a considerable time which indicated that a surface disintegration of the gel with its adsorbed ions had occurred. The granular character of the gel had disappeared, and a more gelatinous material remained in the dialysis cell. Electrodialysis has been used a great deal in this laboratory to purify silica gel, yet the hard granular character of the glassy gel has never been destroyed in the presence of salts except when these complex metal ammonio ions were adsorbed by the gel. It was felt that adsorption isotherms obtained under varying conditions might reveal something of the nature of this unusual ionic adsorption. The investigation here presented gives the preliminary results of the adsorption of silver ammonio complex ions by silica gel, together with a more complete investigation of the adsorption of the tetrammino cupric ion.

EXPERIMENTAL

The silica gel used in this study was the glassy porous variety prepared by the method of Patrick (3). It was washed free of salt and dried at

¹ Presented at the Thirteenth Colloid Symposium, held at St. Louis, Missouri, June 11-13, 1936.

about 100°C. It was then digested in nitric acid, washed, and finally electrodialed for a considerable length of time in an electro dialysis cell. After the resistance of the cell reached a constant high value the gel was removed, dried carefully, and placed in tightly stoppered bottles until used.

In the early part of the study, from 1 to 2 g. of gel was weighed out and added to solutions containing the complex ammonio ions of silver or copper. These solutions were prepared by adding ammonium hydroxide to known concentrations of copper or silver nitrate. Great difficulty was experienced in adding the ammonia solution to the varying strengths of the salt solutions so that the pH of the resulting solution was the same at the time the silica gel was added. Quantitative determinations of the amount of copper and silver present in the solutions before and after the addition of the silica gel made it possible to calculate the amount adsorbed. These early studies gave adsorption isotherms which fitted the Freundlich expression fairly well, but it was recognized that closer control of the pH of the solutions was necessary. It was also decided that other analytical methods would improve the results.

The glass electrode was adopted as the best electrode for determining the pH of the ammoniacal copper nitrate solutions, and it was found to work very well. The Coleman glass electrode was the type used, and it was standardized by the usual buffer solutions. This glass electrode made it possible to obtain electrometric titration curves for the addition of ammonia solutions of copper nitrate. These titration curves determined the pH range of the adsorption studies, as will be discussed later.

The removal of the adsorbed complex copper ions from the silica gel by treatment with 0.5 *N* sulfuric acid was found to be incomplete even after long standing. Experiments with the boiling electrolytic cell as developed by Exner (2) proved that quantitative removal of the copper from the silica gel was possible by this method. The boiling cell of Exner is a simple electrolytic cell consisting of a 300-cc. lipless beaker of the Berzelius type. The cathode consists of a platinum gauze cylinder and the anode consists of two platinum spirals, one inside the cathode and the other outside. A small flame under the beaker causes remarkably vigorous boiling or effervescence, which is undoubtedly aided by the evolution of oxygen at the anodes. Low voltage direct current was applied across the electrodes. During the heating of the cell to boiling a current of 1 ampere was allowed to flow, but this was increased to 6 amperes at 6 volts as soon as boiling had started.

In the present investigation the silica gel containing the adsorbed complex copper ions was removed from the solution in which the adsorption took place and transferred to the electrolytic cell, which contained a solution of 0.5 *N* sulfuric acid. The current was turned on and the removal of the copper from the gel was found to be complete after fifteen minutes of

boiling. An additional hour of treatment showed no additional removal of copper and the gel appeared colorless. The results of a run carried out to determine the time needed for a quantitative experiment are as follows:

Weight of cleaned cathode at beginning of run	10.7587 g.
Weight after 15 minutes boiling	11.1012 g.
Weight after 1 hour additional boiling.....	11.1013 g.
Weight of copper removed from gel	0.3426 g.

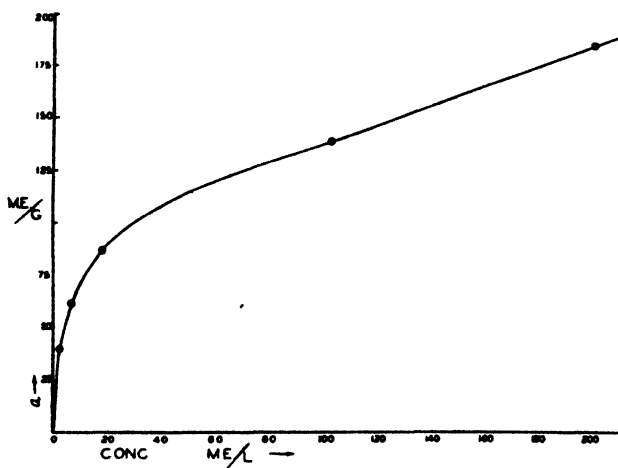


FIG. 1. Adsorption of silver on silica gel²

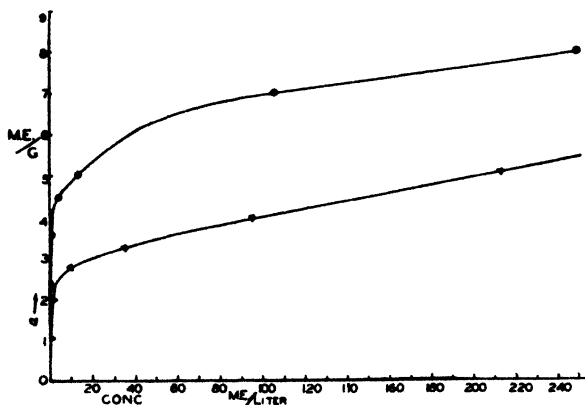


FIG. 2. Adsorption of copper on silica gel

The concentration of the copper complex ion remaining in the solution from which the silica gel had been removed was also determined by the same

² The ordinates of figure 1 are expressed in (M.E./G.) $\times 10$ instead of M.E./G. as shown in the figure.

electrolytic method. In some cases when the concentration of the copper ion originally present before adsorption was low, a precipitate remained undissolved during adsorption. When this was the case the solution was stirred rapidly, decanted from the gel, and filtered. The precipitate was dissolved in sulfuric acid, and the quantity of copper determined in the boiling cell. The total amount of copper obtained on the cathode of the boiling cell from the silica gel, the solution, and the precipitate, if any, checked the concentration of the original solution very well. The boiling cell of Exner is to be recommended as a rapid and accurate quantitative method for the determination of copper.

Using the above methods a series of adsorptions was run at five different pH values. Different concentrations of cupric nitrate solution were placed in a beaker in the presence of the glass electrode, and ammonia solution

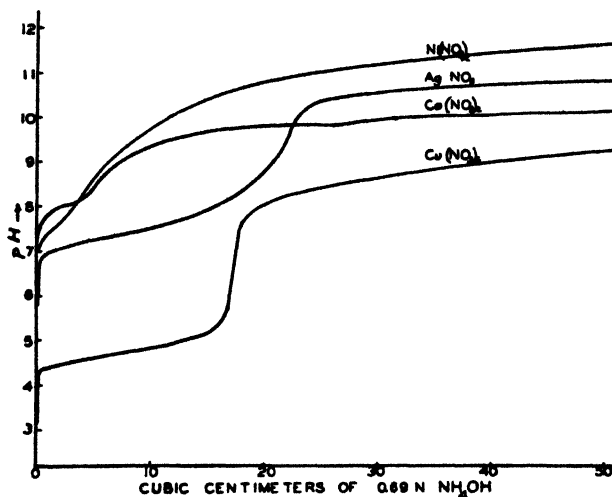


Fig. 3. Titration curves with glass electrode

added until the electrode showed the proper pH. Sufficient time was taken to insure that equilibrium had been reached. The pH was checked occasionally during adsorption, and found to be the same within the limits of error of the glass electrode.

RESULTS AND DISCUSSION

The preliminary results on silver and copper are given in figures 1 and 2. Here the abscissae are milliequivalents per liter of solution and the ordinates are milliequivalents of ion adsorbed per gram of silica gel. The pH values were held as nearly constant as possible. The pH for the upper curve in figure 2 and for silver in figure 1 was something over 10, while the pH for the lower curve in figure 2 was slightly over 7. These results indicated a strong early adsorption of these complex ions.

The potentiometric titration curves using the Coleman glass electrode are shown in figures 3 and 4. Figure 3 gives the titrations of solutions of the same normality of the salts indicated with ammonia solutions. The curves are considerably different for the different salts, and it is intended that

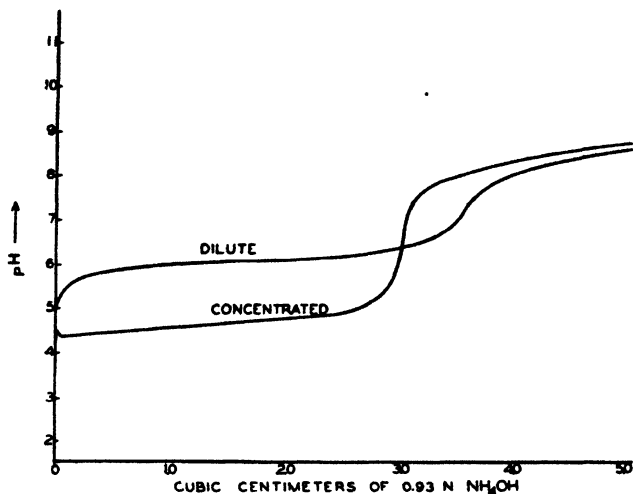


FIG. 4. Ammonia titration curves of cupric nitrate with glass electrode

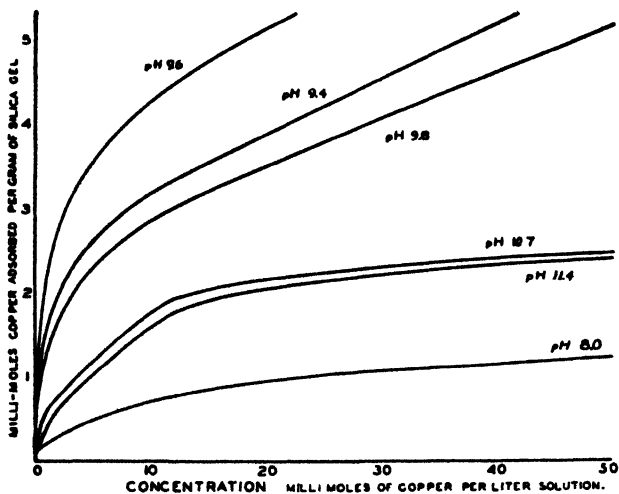


FIG. 5. Adsorption of copper on silica gel at pH values above 8

further study be given to this point. Since it was decided to investigate the adsorption of the complex copper ions first, another set of titrations was run. Figure 4 gives the results of these titrations using the same solution of cupric nitrate in each case, with this difference, that 10 cc. of the solu-

tion was titrated to give the curve marked "concentrated," while the same 10 cc. of solution was diluted to 300 cc. to give the curve marked "dilute." The differences are probably due to changes in activity and hydrolysis.

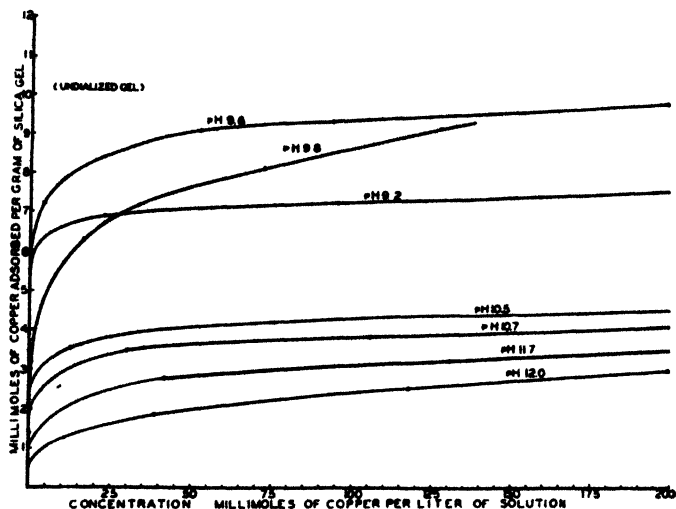


Fig. 6. Adsorption of copper on undialyzed silica gel

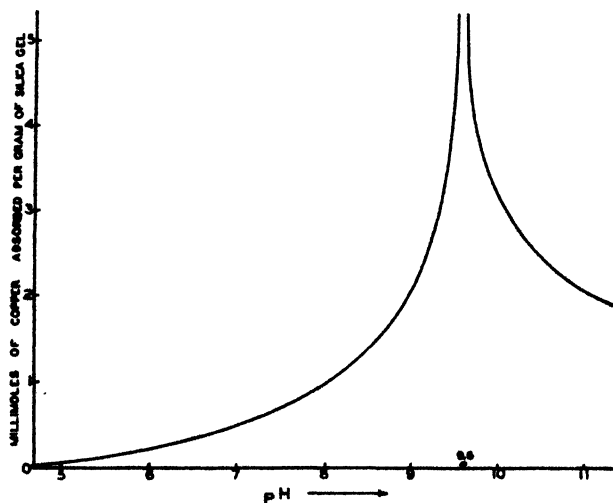


Fig. 7. Adsorption of copper on silica gel from ammoniacal solution

From these results it was evident that the best determination could be made at pH values above the break.

Accordingly, the adsorption measurements were made at pH values above 8. The results of five such adsorption determinations are presented in figure 5. Since the silica gel used in these experiments was electro-

dialyzed, it was decided to use some of the undialyzed gel from the same original source. This gel had been washed thoroughly free of electrolytes by distilled water. The adsorption isotherms for this undialyzed gel are given in figure 6. It is evident that electrodialysis has removed a part of the active surface of the gel as far as this type of adsorption is concerned. It is evident from these results that the pH of the solution plays a vital part in the adsorption of these complex ions. The adsorption reaches a maximum, as is shown in figure 7, at a pH of about 9.6. The character of the silica gel also plays an important part, for the adsorption is much greater on the undialyzed gel than it is on the dialyzed gel. It was felt at first that the silica gel tended to go into solution in solutions of higher pH. This might account for the lowered adsorption above a pH of 9.6. Accordingly a sample of silica gel was placed in a solution of copper ammonio nitrate solution at pH 9.6 and allowed to stand for ten weeks. At the end of this time less than 1 per cent of the silica gel had gone into solution.

TABLE 1
Results obtained in one of the adsorption determinations

EQUILIBRIUM CONCENTRATION OF Cu IN MICROEQUIVALENTS AT EQUILIBRIUM	pH	MILLIMOLES OF Cu ADSORBED PER GRAM OF SILICA GEL
0.37	10 70	0.614
3.12	10 71	0.914
11 75	10 70	1.930
27 72	10 75	2.292
42 23	10 74	2.430

However, this small solubility of silica from the gel may account for the diminished adsorption, provided that the most active part of the surface dissolves.

An example of one of the adsorption determinations is given in table 1. The results here presented indicate that the adsorption is dependent not only on the concentration of the metal ion but also upon the pH of the solution and the character of the silica gel. The whole system is a complex one as has been shown recently by J. Bjerrum (1), who has determined the equilibrium constants for the addition of each successive NH_2 group to the copper. Additional work will be needed to clarify this complex problem further. The adsorption of the first complex copper ammonio ions is apparently strong and irreversible, leading one to suspect that a monomolecular layer of this ion is formed.

SUMMARY

The adsorption of complex ammonio ions has been measured under varying conditions of pH on both electrodialyzed and undialyzed silica gel.

REFERENCES

- (1) BJERRUM, J.: Kgl. Danske Videnskab. Selskab XI, 5 (1931); 10 (1932); and XII, 15 (1934).
- (2) EXNER, F. F.: Private communication to the authors. This work was presented at the 1936 Spring Meeting of the Minnesota Academy of Science.
- (3) PATRICK, W.: U. S. patent 1,297,724.
- (4) SMITH, G., AND REYERSON, L. H.: J. Am. Chem. Soc. **52**, 2584 (1930).

FACTORS INFLUENCING ADSORPTION AT SURFACES OF RED CELLS¹

BETTY R. MONAGHAN AND H. L. WHITE

*Department of Physiology, Washington University School of Medicine,
St. Louis, Missouri*

Received June 11, 1936

We have recently shown (4) that the aggregation (as measured by sedimentation velocity) of red cells brought about by plasma globulins and by other proteins, as gelatin and casein, is not accompanied by an adsorption of these proteins at the cell surface. The proteins presumably act by depriving the red cells of adsorbed water, thus increasing their surface energy and tendency to aggregate. It was in fact shown that normal red cells do not adsorb non-specific proteins even in high concentrations; that the electrophoretic mobility of the cell, characteristic for each species, is determined by the composition of the cell membrane itself and is unchanged by washing away plasma proteins or even by thorough washing of hemolyzed cells in alkaline solution (6).

Bellis and Scott (2) report results which they interpret as indicating that considerable amounts of plasma protein are normally adsorbed on red cells. Dilution of the plasma with isotonic solutions removes some of this adsorbed protein, whereas dilution with hypertonic solutions causes a further adsorption of protein by the red cell. Their interpretation is directly opposed to the conclusions of Abramson (1) and ourselves that normal red cells do not adsorb plasma proteins.

The objects of the present paper are (1) to test the experimental evidence offered by Bellis and Scott for the adsorption of plasma proteins by normal red cells, (2) to investigate the conditions under which the surface of the red cells may become damaged, as evidenced by a decreased sedimentation velocity, and the result of such damage on the ability of the cells to adsorb proteins, and (3) to investigate the effect of lecithin on the charge and sedimentation velocity of normal cells.

¹ Presented before the Thirteenth Colloid Symposium, held at St. Louis, Missouri, June 11-13 (1936).

This work was aided by a grant from the Rockefeller Foundation to Washington University for research in science.

EXPERIMENTAL

1. Adsorption of plasma proteins by normal red cells

According to the findings of Bellis and Scott the dilution of defibrinated beef blood with isotonic salt or sugar solution results in a higher concentration of protein in the supernatant fluid than is calculated from the known dilution of the plasma, allowing for changes in the volume of the cells as determined by hematocrit readings. The protein increase is proportional to the amount of dilution; with their greatest dilution (70 parts of isotonic salt to 30 of blood) it amounts to 1.3 g. per 100 cc. of serum. This means that the cells (approximately 60 cc.) contained in 100 cc. of serum give up to the surrounding medium 1.3 g. of presumably adsorbed protein, or 1 cc. of cells gives 0.022 g. of protein. A similar dilution of whole blood with hypertonic salt or sugar resulted, on the other

TABLE 1
Nitrogen in the supernatant fluid from packed cell mass

EXPERIMENT NO.	NaCl CONCENTRATION	NITROGEN IN SUPERNATANT FLUID	PROTEIN (N \times 6.25) IN SUPERNATANT FLUID
	<i>per cent</i>	<i>mg. per cent</i>	<i>per cent</i>
1 (beef).....	0.9	113	0.70
	8.1	90	0.56
2 (beef).....	0.9	99	0.61
	8.1	102	0.63
3 (dog).....	0.9	40	0.25

hand, in a taking up of approximately 0.005 g. of protein per cubic centimeter of cells.

We have tested these conclusions in the following way. Instead of diluting the whole blood and depending upon hematocrit readings in the diluted media for true dilution values, we have added the salt solution directly to the packed cells. Fresh defibrinated beef blood was centrifuged for one and one-half hours at 3200 R.P.M. Unfortunately this was the highest speed obtainable with the available centrifuge when loaded with two 15-cc. tubes; undoubtedly better packing of the cells could be obtained with higher centrifugal speeds. The serum was drawn off and to one volume of packed cells was added one volume of isotonic (0.9 per cent) or hypertonic (8.1 per cent) sodium chloride solution. The cells were thoroughly mixed with the salt solution and allowed to stand for thirty minutes. The tubes were again centrifuged and the total nitrogen in

the supernatant fluid determined by a micro-Kjeldahl method.² According to the calculations given above from the data of Bellis and Scott, assuming that no serum remained in the packed cell mass, the supernatant fluid in the case of the isotonic salt should contain at least 2.2 per cent protein, while the hypertonic washing fluid should contain no protein. Several such experiments on beef cells gave the results shown in table 1. Calculating all the nitrogen as protein the supernatant isotonic fluid contained less than one-third of the protein predicted on the basis of the results of Bellis and Scott. There is in fact even less protein in our supernatant fluid than the figures indicate, since 7 to 10 mg. of nitrogen per 100 cc. of supernatant fluid are in the urea from the cells. Since the hypertonic fluid contained practically the same protein concentration, it is evident that this protein must have been derived from serum remaining in the packed cell mass and not from protein adsorbed on the cells. If the original serum contained 8 per cent protein, this would mean that under the conditions of the experiment about 8 per cent of the packed cell volume consisted of serum, a not unreasonable figure considering the relatively low centrifugal speed at which the cells were packed. It seemed desirable to repeat the experiment on a type of blood in which the cells form large aggregates and would thus be expected to pack better at a given centrifugal speed. The results on dog cells are shown in table 1. Since appreciable hemolysis occurred in the hypertonic salt, only the isotonic was analyzed. If all the nitrogen is calculated as protein we obtain 0.25 per cent protein in the supernatant fluid, which means that in this case about 3 per cent of the packed cell mass consisted of serum.

2. *Effect of prolonged standing and of washing on the surfaces of the red cells*

It was emphasized in earlier publications (4, 6) that in order to obtain correct values for the sedimentation velocity of red cells, fresh cells (not more than three to four hours old) must be used. Allowing cells to stand for long periods or washing them with buffered isotonic sugar markedly decreased the sedimentation velocity. We have here made a more quantitative investigation of the conditions under which cells lose their capacity for rouleau formation. Dog cells, which were shown to have the highest sedimentation velocity and the highest electrophoretic mobility at pH 7.4, were used.

The sedimentation experiments of this section were carried out in a 1 per cent gelatin solution (Eastman's) made up in *M*/50 phosphate buffer (pH 7.4) plus 0.9 per cent sodium chloride. The pH of the buffer was not significantly changed by this concentration of gelatin. The cells were centrifuged for 15 minutes at 2000 R.P.M. and two volumes of the gelatin

* We are indebted to Dr. W. B. Wendel for the nitrogen determinations.

solution were added to one volume of packed cells. The thoroughly mixed cell suspensions were sucked up into glass tubes of 3.5 mm. bore and 35 cm. long. The tubes bore short segments of rubber tubing on their lower ends, which, after filling, were closed with spring clips. The number of millimeters which the cells sank in a specified time was then measured. The sedimentation velocity is of course a direct measure of the degree of aggregation of the cells.

Electrophoretic determinations were carried out with a microscopic electrophoresis cell, using the technique previously described (7). The medium in which the cells were suspended was *M*/50 phosphate buffer (pH 7.4) plus 0.3 per cent sodium chloride plus 6 per cent sucrose. The proteins studied were dissolved in this medium. Sugar was substituted for part of the salt in order to cut down the current density. These determinations were made with the idea of detecting any adsorption of

TABLE 2

Effect of standing on protein adsorption and sedimentation velocity of dog red cells

	MOBILITY IN MICRA PER SECOND PER VOLT PER CENTIMETER			SINKING IN 1 PER CENT NORMAL GELATIN IN 30 MINUTES
	Autoge- nous plasma diluted 1 to 200	0.01 per cent normal gelatin	0.01 per cent iso- electric gelatin	
				<i>mm.</i>
Fresh dog cells	1 52	1 53	1 55	113
After standing 1 day	1 52	1 54	1 54	59
After standing 2 days	1 46	1 51	1 50	30
After standing 4 days	1 45	1 48	1 48	13
Protein-coated glass particles	0 65	0 61	0	

protein which might occur at the red cell surface. The electrophoretic mobility of the dog red cell is several times that of any of the proteins studied (as measured by the mobility of glass particles covered with these proteins). An adsorption of protein would therefore lower the red cell mobility; a complete coat would lower the mobility to that of the protein itself. Mobility determinations were made in diluted dog plasma, ordinary gelatin (Eastman) having an isoelectric point at pH 4.7, and a sample of gelatin obtained from the Heil Company which was found to have an isoelectric point at pH 7.4.

As previously stated, allowing cells to stand in the ice box for long periods of time in their own serum or plasma decreases their sedimentation velocity. The decrease in sedimentation velocity for a given time of standing is, however, very irregular. Some samples of cells are cut down to a very small fraction of their original sedimentation velocity on twenty-four hours' standing. Other samples may require a week for the same change.

The change is not correlated with hemolysis; samples which show no hemolysis may show a very great decrease in sedimentation, and others which show considerable hemolysis on standing may have a normal sedimentation rate. In table 2 the sinking velocity in 1 per cent gelatin and mobility in various proteins of a sample of dog cells has been followed over a period of four days. The oxalated whole blood was allowed to stand in the ice box. Samples were removed each day and centrifuged, the packed cells being resuspended in the protein solutions. It is evident that a marked decrease in sedimentation velocity may take place before any measurable adsorption of protein has occurred.

Table 3 shows the effects of washing dog cells in isotonic salt and sugar.

TABLE 3

Effect of washing on protein adsorption and sedimentation velocity of dog red cells

CELLS	MOBILITY IN MICRA PER SECOND PER VOLT PER CENTIMETER				SINKING IN 1 PER CENT NORMAL GELATIN IN 30 MINUTES
	Buffer	0.01 per cent iso- electric gelatin	Autog- enous plasma diluted 1 to 200	1 per cent normal gelatin	
Fresh normal dog cells	1 55	1 56		1 44	90
After washing in 0.9 per cent NaCl . .	1 57	1 56			89
After standing 3 days in 0.9 per cent NaCl .		1 56			21
After standing 3 days in serum		1 53			2
After washing in 10 per cent sucrose .	1 58	1 38			0
After rapid washing in 10 per cent sucrose			1 54		3
After standing overnight in 10 per cent sucrose		1 55	1 56	1 22	2
After rapid washing in 5 per cent dextrose			1 56		1
After standing overnight in 5 per cent dex- trose		1 54	1 58	1 25	2
Washed ghosts	1 54	0 99			

The data show that washing cells in 0.9 per cent sodium chloride solution has no immediate effect either on their sedimentation velocity or on their ability to adsorb gelatin. Also, cells allowed to stand in 0.9 per cent sodium chloride retain their ability to aggregate in gelatin solutions at least as long as cells which are allowed to stand in their own serum or plasma. Cells washed in isotonic sucrose, on the other hand, always show a great decrease in sedimentation velocity, which may or may not be accompanied by a measurable adsorption of protein from very dilute protein solutions. This has been found to be true also for the cells of other species (horse and human). Washing with isotonic dextrose gives similar results; as shown in table 3, cells may not adsorb protein after such washing but we have

observed adsorption of gelatin, casein, and egg albumin from 0.01 per cent solution of these proteins at pH 7.4 by horse cells washed in isotonic dextrose. Hemolyzed cells washed free of hemoglobin (6) adsorbed protein still more readily.

It is to be noted, however, that irrespective of their treatment all dog cells, including the washed ghosts, have the same mobility in the absence of protein. That is, the change or damage to the cell surface which allows it to adsorb protein is not accompanied by any change in the electrophoretic properties of the cell in the absence of protein. Cells treated with isotonic sucrose or dextrose may not be altered sufficiently to adsorb measurable amounts of gelatin or plasma protein from dilute protein solution and will yet adsorb a measurable amount of gelatin from 1 per cent gelatin, the concentration in which the sedimentation velocities have been determined. This is shown by the findings in table 3 that cells after treatment with isotonic sucrose or dextrose adsorbed gelatin from 1 per cent solution (as evidenced by their lower mobility in 1 per cent gelatin than was that of fresh cells in 1 per cent gelatin), although they did not adsorb measurable amounts of protein from dilute gelatin or plasma.

Whether or not the adsorption of the protein by the red cells is the cause of the decreased ability to aggregate is not known; both phenomena may be separate manifestations of some unknown change in the physical state of the cell surface. It seems evident that the common practice of washing red cells with isotonic sugars prior to studies on their ability to adsorb specific antibodies is not without danger, since such washing may damage the cell surface in such a way that it is capable of adsorbing non-specific proteins. Washing with isotonic salt solution is to be preferred.

3. Effect of lecithin on charge and on sedimentation velocity

Kürten (3) and Theorell (5) report a decrease in sedimentation velocity of whole blood on the addition of lecithin. Both authors ascribe this stabilizing effect to a direct action on the cells; they assume an adsorption of lecithin at the cell surface with a resulting increase in charge.

We have investigated the effect of added lecithin on the sedimentation rate of dog red cells both in their own plasma and in 1 per cent gelatin. To our 1 per cent gelatin solution (made up as previously described in *M/50* phosphate buffer plus 0.9 per cent sodium chloride) was added 0.05 per cent of egg lecithin (Pfanstiehl). The pH of the buffer was not significantly changed by this concentration of lecithin. Dog cells in the 1 per cent gelatin solution alone sank 113 mm. in 30 minutes; in the gelatin plus suspended lecithin they sank less than 1 mm. in the same time. Dog cells in their own plasma sank 51 mm. in 1 hour; in plasma plus 0.05 per cent of added lecithin they sank 8 mm. in 1 hour.

Electrophoresis determinations, however, demonstrate that the lecithin acts by a very different mechanism from that postulated by Kürten and by Theorell. The mobility of the dog red cell in the buffer-sucrose-sodium chloride medium is approximately 1.55 micra per second per volt per centimeter. When a dilute cell suspension and lecithin are mixed (in the absence of any dissolved protein) the cells become attached to the particles of lecithin and the mobility is intermediate between that of cells and that of lecithin. When more cells are added (the suspension is still much less dense than that used in sedimentation experiments) the mobility becomes that of the normal cells, the larger particles of lecithin being completely surrounded by "adsorbed" cells. In a 1 per cent gelatin solution made up in the same medium the mobility of the cells is 1.41 micra per second per volt per centimeter. This decrease in mobility in concentrated gelatin is due to increased viscosity in the double layer, not to adsorption of gelatin (6). The mobility of the lecithin particles in a 1 per cent gelatin solution becomes the same as that of the gelatin itself, approximately 0.5 micra per second per volt per centimeter; i.e., the lecithin is completely coated with gelatin. When the cells and lecithin are mixed in the presence of 1 per cent gelatin, the cells are seen to move at exactly the same rate as in the absence of lecithin, 1.40 micra per second per volt per centimeter. The lecithin particles, which can easily be distinguished from the cells, move at the same rate as gelatin, 0.5 micra per second per volt per centimeter. Obviously, the action of the lecithin in decreasing sedimentation velocity in the presence of protein is not due to an adsorption of lecithin and increased charge on the cells, but rather to a binding of the protein by the lecithin, resulting in a decrease in the effective concentration of protein. The fact that the same concentration of lecithin has a much greater effect on sedimentation velocity in 1 per cent gelatin than in plasma is presumably to be explained on the basis that a given concentration of lecithin binds a smaller fraction of the protein present in plasma than in 1 per cent gelatin.

SUMMARY

1. The conclusion of Bellis and Scott that beef red cells are normally coated with plasma proteins is not confirmed. Normal cells do not adsorb measurable quantities of gelatin or of plasma proteins.

2. Cells allowed to stand in the ice box in their own plasma or in 0.9 per cent sodium chloride gradually lose their ability to form rouleaux in gelatin solutions, as shown by a decreased sedimentation velocity. This change is accelerated by washing the cells in isotonic sugar and may be accompanied by a slow and incomplete adsorption of protein at the cell surface.

3. Small quantities of added lecithin inhibit the sedimentation of dog

cells in plasma or gelatin. This inhibition is due to an adsorption of protein by the lecithin, thus decreasing the effective protein concentration, not to a direct effect of the lecithin on the surface of the red cells.

REFERENCES

- (1) ABRAMSON, H. A.: *J. Gen. Physiol.* **12**, 469 (1929).
- (2) BELLIS, C. J., AND SCOTT, F. H.: *J. Biol. Chem.* **111**, 17 (1935).
- (3) KÜRTEH, H.: *Arch. ges. Physiol.* **185**, 248 (1920).
- (4) MONAGHAN, B. R., AND WHITE, H. L.: *J. Gen. Physiol.* **19**, 715 (1936).
- (5) THEORELL, H.: *Biochem. Z.* **223**, 1 (1930).
- (6) WHITE, H. L., AND MONAGHAN, B. R.: *Am. J. Physiol.* **115**, 31 (1936).
- (7) WHITE, H. L., AND MONAGHAN, B. R.: *J. Biol. Chem.* **113**, 371 (1936).

THE MECHANISM OF THE COAGULATION OF SOLS BY ELECTROLYTES. VI

CUPRIC FERROCYANIDE SOL¹

HARRY B. WEISER AND W. O. MILLIGAN

Department of Chemistry, The Rice Institute, Houston, Texas

Received June 11, 1936

A mechanism to account for the coagulating action of electrolytes on hydrophobic sols has been proposed as a result of investigations on sols of the hydrous oxides of iron (9, 15), aluminum (11), chromium (10), of arsenic trisulfide (13), and of sulfur (14). For the sake of clarity the essential points of the proposed mechanism will be illustrated by a specific example: (a) The micelles of a ferric oxide sol are, in general, positively charged, owing to preferential adsorption of ferric and hydrogen ions from the intermicellar solution. These ions form the inner portion of a double layer, the outer portion of which is a Gouy diffuse layer, usually of chloride ions. (b) A part of the chloride ions in the diffuse outer layer are attracted (adsorbed) to the inner layer so strongly that they cannot be detected potentiometrically, whereas the remainder, because of their relatively higher kinetic energy, exert sufficient osmotic force against the electrical attraction of the inner layer that they are a part of the intermicellar solution, and so are measurable potentiometrically. (c) On adding to the sol an electrolyte such as potassium sulfate, the sulfate ions, being more strongly adsorbed than the chloride, take up a position closer to the inner layer of adsorbed hydrogen and ferric ions. This diminution in thickness of the double layer causes a decrease in the potential on the particles; when the potential is reduced sufficiently, coagulation results. (d) The adsorption of sulfate is accompanied by a displacement of adsorbed chloride from the innermost portion of the outer layer. (e) The difference between the chloride concentration before and after the addition of sulfate (in other words the displaced chloride) is not equivalent to the adsorbed sulfate, since a part of the sulfate which enters the layer corresponds to chloride in the intermicellar solution of the original sol. (f) The order of magnitude of the adsorption of similar ions of the same valence such as sulfate, oxalate, and chromate is the same; hence they possess a

¹ Presented before the Thirteenth Colloid Symposium, held at St. Louis, Missouri, June 11-13, 1936.

similar capacity to displace chloride and a similar coagulating power. (g) Ions such as ferricyanide, with three charges, are drawn closer to the inner layer than the divalent ones. Hence less of a trivalent ion needs to be adsorbed than of a divalent ion to reduce the potential on the particles to the same value. (h) The adsorption necessary to reduce the potential on the particles to the point of coagulation is less for trivalent ions than for divalent ions; and the displacement of chloride ions at the coagulation point is less with the former than with the latter. (i) Univalent ions, such as nitrate ion, are attracted toward the inner layer (adsorbed) much less strongly than multivalent ions; hence the potential on the particles is lowered much less for the same concentration of nitrate ion than for sulfate or ferricyanide ions. The displacement of chloride by nitrate is much less than for an equivalent amount of multivalent ions, since chloride is adsorbed somewhat more strongly than nitrate at the same concentration.

Although the adsorption mechanism proposed to account for the action of electrolytes on hydrophobic sols was suggested from observations of the advantages and limitations of the well-known Freundlich theory, the categorical statement of Verwey and Kruyt (6, 7) that "The Weiser theory does not differ essentially from that of Freundlich" is not justified. As a matter of fact, sixteen years ago the author (8) was the first to point out that one of the fundamental concepts of Freundlich's original theory was not supported by experiment, namely, that the adsorption of ions of varying valence is equivalent at the precipitation concentration of the ions. This has since been recognized by Freundlich (1) himself. The mechanism proposed above not only accounts for the variation from equivalent adsorption at the coagulation concentration of ions of varying valence, but also suggests why equivalent adsorption of ions of varying valence is unnecessary to effect precipitation at the varying precipitation concentrations. In the proposed mechanism, the reduction in the potential at the surface of the particles on adding electrolytes is attributed to a contraction of the double layer as a result of adsorption of the precipitating ions. Verwey and Kruyt accept Müller's (4) point of view and conclude that the lowering of the ζ -potential is "merely due to 'compression' of the diffuse outer layer and a subsequent increase of the capacity of this part of the double layer" (7). Since, in general, the thickness of the inner layer of the double layer is changed but little on the addition to sols of small amounts of electrolytes with high coagulating power, it follows that the decrease in thickness of the double layer, to which we have attributed the lowering of the ζ -potential, implies a compression of the outer layer. Hence it would appear that our point of view differs from that of Verwey and Kruyt chiefly in that the contraction of the double layer or compression

of the outer layer is believed by us to result from adsorption of precipitating ions, whereas Verwey and Kruyt consider that adsorption is neither a necessary nor a sufficient cause of potential reduction at the surface of the particles. The conclusions of Verwey and Kruyt were based on the results of their important investigations with negative silver iodide sol (6, 7). With this sol it is claimed (a) that in some cases complete adsorption occurs at much lower concentrations than corresponds to the flocculation value, and (b) that in other cases flocculation occurs long before sufficient electrolyte is added to reach the maximum adsorption. An example of the first behavior is the adsorption of UO_2^{++} by a sol containing 75 g. of silver iodide per kilogram of sol. The precipitation value was 4 milliequivalents per kilogram of sol, but the maximum adsorption of 0.23 milliequivalent was reached when only 0.5 milliequivalent was added. In these adsorption studies Verwey and Kruyt determined the amount taken by analyzing the ultrafiltrates. Since ultrafiltration of a sol influences the adsorption equilibria, it is questionable whether the composition of the intermicellar solution should be deduced from an analysis of the ultrafiltrate. In this connection McBain and McClatchie (3) showed that the hydrogen-ion concentration of the ultrafiltrate from a ferric oxide sol varies many fold with the rate of ultrafiltration.

That flocculation may occur long before enough electrolyte is added to reach the maximum adsorption is illustrated by the flocculation of a silver iodide sol by adsorption of a very small amount of Ce^{+++} in the presence of a large excess of H^+ . Thus an undialyzed sol containing 80 millimoles of silver iodide, 80 millimoles of nitric acid, and 8 millimoles of hydriodic acid per liter adsorbed little or no cerium at the coagulation value. In this case the combined adsorption of Ce^{+++} and H^+ , chiefly the latter, accounts for the reduction of the ζ -potential to the coagulation point. Moreover, Verwey and Kruyt always observed a marked retrograde adsorption or falling-off of adsorption above the coagulation point, which they attributed to "a decrease in surface caused by a secondary change in the coagulum" (6). This factor may be, in part, responsible for the low adsorption of cerium under the above conditions.

The silver iodide sol is a comparatively simple system containing highly disperse silver iodide particles, which are negatively charged owing to preferential adsorption of iodide ions from the highly ionized hydriodic acid. Since this sol appears to behave differently in certain respects from the series of sols investigated in this laboratory, it seemed advisable to study the behavior of a sol of similar structure on the stepwise addition of electrolytes. The sol chosen was cupric ferrocyanide sol, which is negatively charged owing to preferential adsorption of ferrocyanide ions from the highly ionized hydroferrocyanic acid.

FORMATION OF CUPRIC FERROCYANIDE SOL

Preparation of $\text{H}_4\text{Fe}(\text{CN})_6$. Pure cupric ferrocyanide is best prepared by the interaction of hydroferrocyanic acid and a cupric salt (5, 9). The gel, as ordinarily prepared from potassium ferrocyanide and a cupric salt, contains more or less of the potassium salt. Since it was essential in the present work to avoid the presence of cations other than hydrogen and copper, hydroferrocyanic acid was always employed in preparing the gel. The acid was prepared as follows: 100 g. of potassium ferrocyanide was dissolved in 500 cc. of water freshly boiled to remove dissolved oxygen. The solution was cooled to 10°C ., and slightly more than an equivalent amount of concentrated hydrochloric acid was added. Any potassium chloride which precipitated was dissolved by adding a little water; then 125 cc. of cold ether was poured slowly into the bottle, which was shaken gently with a whirling motion in order to bring the ether slowly in contact with the solution. By this procedure a hydroferrocyanic acid-ether compound was precipitated as a coarse, crystalline mass which was transferred rapidly to a Büchner funnel and washed, first with a mixture of dilute hydrochloric acid and ether, and finally with pure ether. After the crystals were dry, they were transferred to a flask and dissolved in 250 cc. of absolute alcohol. The small amount of potassium chloride adsorbed by the crystals was insoluble in the alcohol and was filtered off. The solution was next mixed with absolute ether and the resulting crystals were transferred to a Büchner funnel and washed with absolute ether. The compound was then placed in a vacuum desiccator over sulfuric acid and evaporated with a water pump until most of the ether was removed, after which a high vacuum was maintained by the continuous operation of an oil pump for thirty-six hours. The resulting product was pure white and was quite stable in the absence of moisture.

Preparation of $\text{Cu}_2\text{Fe}(\text{CN})_6$ gel. Sufficient hydroferrocyanic acid to make 2 g. of gel was dissolved in 200 cc. of water in an 800-cc. beaker and an equivalent amount of pure cupric acetate in 200 cc. of water was placed in a separatory funnel. The copper solution was allowed to run slowly into the hydroferrocyanic acid solution, which was stirred vigorously with a motor-driven stirrer. Since the gel was found to peptize most easily if an excess of copper was avoided, the precipitation was brought to completion carefully in the following way: after approximately 95 per cent of the necessary copper solution was added, the mixture was transferred to two 250-cc. Pyrex bottles and centrifuged in a No. 1 International Equipment Company centrifuge at 3000 R.P.M. for 5 minutes. Since most of the cupric ferrocyanide remained in the sol state in the presence of the excess hydroferrocyanic acid, copper solution was added to the bottles in 2-, 1-, and 0.5-cc. portions with intermediate centrifuging until the gel was thrown down and, finally, dropwise until the supernatant solution was clear or

only slightly turbid. After the gel was well matted down by centrifuging, the supernatant liquid was poured off and the gel was washed in the following way: approximately 100 cc. of water was added to each of the bottles, which were shaken vigorously to break up the gel thoroughly. The bottles were then filled with water; after shaking they were centrifuged as before. Again a considerable portion of the gel was peptized to the sol state, and copper solution was added dropwise with intermediate centrifuging until the supernatant solution was almost clear. This was poured off and the washing was repeated two more times by the same procedure. In this way a 1-g. portion of cupric ferrocyanide was washed three times with 250-cc. portions of water, thereby removing the reaction product, acetic acid, almost completely.

Peptization of $\text{Cu}_2\text{Fe}(\text{CN})_6$ gel. The 2 g. of washed gel was suspended in approximately 100 cc. of water, and sufficient hydroferrocyanic acid was added to make a solution between 0.001 and 0.002 *N*. After shaking at intervals for an hour or two, the mixture was allowed to stand. The resulting sol was quite clear and deep red in color. The small amount of unpeptized solid was removed by centrifuging, and the sol was ready for the titration and adsorption studies. Since hydroferrocyanic acid is instable in contact with water, undergoing an internal oxidation-reduction reaction with the formation of Prussian blue and hydrocyanic acid, it might be expected that the sol would be quite unstable; but this is not the case. Although free hydroferrocyanic acid is quite unstable, the adsorbed acid is stable. Sols prepared by the above method have stood for weeks without appreciable sedimentation. Of course, any unadsorbed hydroferrocyanic acid in the intermicellar solution will decompose gradually, but in the sols prepared as above described, only a little excess hydroferrocyanic acid was present. In any event, sols which had stood three or four days underwent no change in hydrogen-ion concentration during the course of the experiments.

TITRATION AND ADSORPTION EXPERIMENTS

The stepwise addition of electrolytes to sols and the measurement of the accompanying change in concentration of "counter ions" is termed titration.

The method of procedure employed in the present investigation was similar to that described in former papers in this series: 20 cc. of sol was placed in the outer compartment of an all-glass mixing apparatus and a definite volume of electrolyte diluted to 5 cc. in the inner compartment. The electrolyte and water were measured with calibrated 2-cc. Mohr pipets graduated in 0.01 cc. After thorough shaking, the mixture was transferred to 50-cc. Pyrex flasks and allowed to stand four hours. The hydrogen-ion concentration was determined by means of the glass elec-

trode, using a Youden apparatus with a glass-bulb electrode prepared with Corning 015 glass.

The adsorption of barium and strontium ions, at or above the precipitation concentration for the sol, was determined as follows: 50- or 60-cc. portions of sol were precipitated in Pyrex bottles under the same condi-

TABLE 1
Titration of sol I

0.02 N BaCl ₂ ADDED TO 20 CC. OF SOL. TOTAL VOLUME, 25 CC.	[H ⁺] × 10 ³ IN SOLUTION	[H ⁺] × 10 ³ DISPLACED	[Ba ⁺⁺] ADDED	[Ba ⁺⁺] × 10 ³ ADSORBED
0.0	1.29	0.0	0.0	
0.5	1.50	0.21	0.4	
1.0	1.68	0.39	0.8	
1.5	2.03	0.74	1.2	
2.0	2.10	0.81	1.6	
2.5	2.19	0.90	2.0	
3.0	2.19	0.90	2.4	2.22
4.0	2.19	0.90	3.2	
5.0	2.19	0.90	4.0	2.84

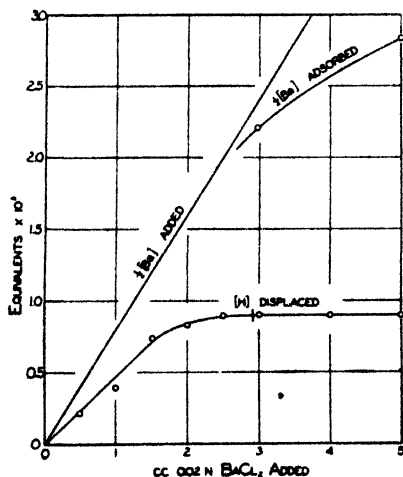


FIG. 1. Curves for adsorption of Ba⁺⁺ and displacement of H⁺ in the titration of cupric ferrocyanide sol I with barium chloride.

tions as described above, and after standing four hours, the mixture was centrifuged and 50-cc. samples of the supernatant liquid were taken for analysis. The barium and strontium were determined as sulfate following standard methods of procedure:

Experiments with sol I. The experiments were limited to salts of the alkalis and alkaline earths, since the ferrocyanides of the other metals are

insoluble. After preliminary work had demonstrated the applicability of the experimental technique to the case at hand, observations were made of the hydrogen-ion displacement and adsorption of barium ion on titrating a sol containing 18 g. of cupric ferrocyanide per liter with 0.02 *N* barium chloride. The results are shown in table 1 and are reproduced graphically in figure 1. It is apparent that the displacement of hydrogen ions is less than the amount of barium added and of barium adsorbed. The dis-

TABLE 2
Titration of sol II

0.02 <i>N</i> BaCl ₂ ADDED TO 20 CC. OF SOL. TOTAL VOLUME, 25 CC.	[H ⁺] × 10 ³ IN SOLUTION	[H ⁺] × 10 ³ DISPLACED	[Ba ⁺⁺] ADDED	[Ba ⁺⁺] × 10 ³ ADSORBED
0.0	0.85	0.0	0.0	
0.5	0.98	0.13	0.4	
1.0	1.10	0.25	0.8	
1.5	1.34	0.49	1.2	
2.0	1.34	0.49	1.6	
2.5	1.34	0.49	2.0	1.65
5.0	1.34	0.49	4.0	2.31

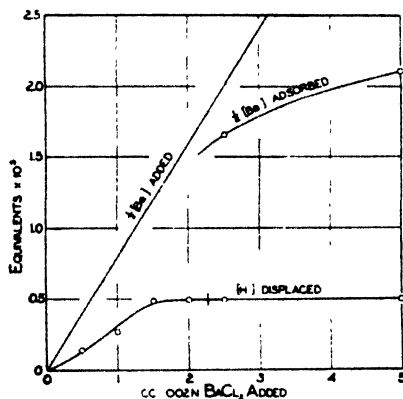


FIG. 2. Curves for adsorption of Ba⁺⁺ and displacement of H⁺ in the titration of cupric ferrocyanide sol II with barium chloride.

placement is complete somewhat below the precipitation value, indicated by a vertical line cutting the displacement curve. Most of the added barium is adsorbed at concentrations just above the precipitation value.

Experiments with sol II. A second sol was prepared using but one-half the amount of hydroferrocyanic acid to effect the peptization as was used in sol I; it contained 13 g. of cupric ferrocyanide per liter. The observations of displacement of hydrogen and adsorption of barium on titrating with barium chloride are given in table 2 and figure 2. As was to be

expected, the hydrogen-ion concentration of the sol at the start was less than for sol I and the amount of hydrogen ion displaced by the added electrolyte was correspondingly less.

Experiments with sol III. For the purpose of comparing the action of different electrolytes, a third sol of hydrogen-ion concentration intermediate between I and II and containing 16 g. of cupric ferrocyanide per

TABLE 3
Titration of sol III

ELECTROLYTE ADDED TO 20 CC OF SOL. TOTAL VOLUME, 25 CC.	$[H^+] \times 10^8$ IN SOLUTION	$[H^+] \times 10^8$ DISPLACED	EQUIVALENTS $\times 10^8$ ADDED	EQUIVALENT $\times 10^8$ ADSORBED
0.02 N BaCl ₂			$\frac{1}{2}[Ba^{++}]$	$\frac{1}{2}[Ba^{++}]$
0 0	0 97	0 0	0 0	
1 0	1 15	0 18	0 8	
1 5	1 19	0 22	1 2	
2 0	1 26	0 29	1 6	
2 5	1 29	0 32	2 0	
2 8			2.24	1.74
3.0	1 29	0 32	2 4	
5 0	1 29	0 32	4 0	2 07
0.02 N SrCl ₂			$\frac{1}{2}[Sr^{++}]$	$\frac{1}{2}[Sr^{++}]$
0.0	0 97	0 0	0 0	
1 0	1 08	0 11	0 8	
1 5	1 13	0 16	1 2	
2 0	1 22	0 25	1 6	
2 5	1 24	0 27	2 0	
2 8			2 24	1 55
3.0	1 26	0 29	2 4	
4.0	1 26	0 29	3 2	
5 0			4 0	1.72
0.033 N KCl			$[K^+]$	
0.0	0 97	0 0	0 0	
1 0	1 08	0 11	1 33	
2.0	1 15	0 18	2 67	
3 0	1 19	0 22	4 00	
4.0	1 19	0 22	5.33	
5.0	1 19	0 22	6 67	

liter was titrated with the chlorides of barium, strontium, and potassium; and the adsorption of barium and strontium was determined. The data are given in table 3 and figure 3. It is apparent that the coagulating power, displacing power for hydrogen ion, and the adsorption of strontium and barium are similar, but the values for strontium are somewhat less in every case than for barium. The univalent potassium ion has a definitely

lower coagulating power than the divalent ions, and the power of the former to displace hydrogen ions is lower at the same concentration.

DISCUSSION OF RESULTS

The behavior of cupric ferrocyanide sols towards electrolytes is so much like that of the hydrous oxide and sulfur sols, that it can be explained by a similar mechanism. Cupric ferrocyanide gel peptized by hydroferrocyanic acid is negatively charged, owing to preferential adsorption of the common ferrocyanide anion. Since the ionization constant of the fourth hydrogen ion is so small (2), it is probable that even in the dilute

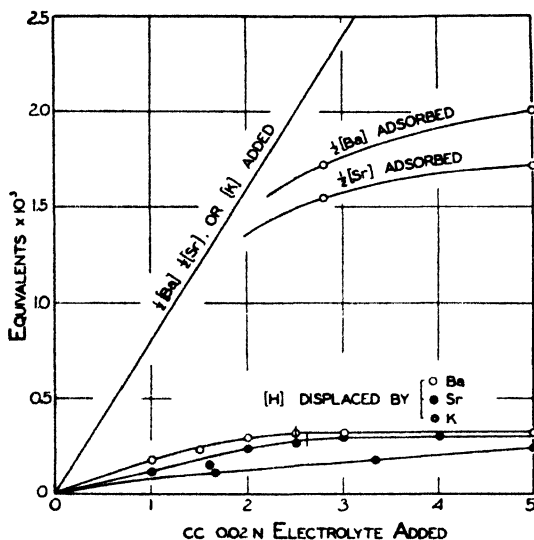


FIG. 3. Curves for adsorption of precipitating cations and displacement of H^+ in the titration of cupric ferrocyanide sol III with the chlorides of barium, strontium, and potassium.

solutions employed, the anion is chiefly $HFe(CN)_6^{4-}$ (represented by R^{4-} in figure 4) rather than $Fe(CN)_6^{4-}$. In any event, the negative ions may be assumed to form the inner portion of a double layer surrounding the hydrous particles of cupric ferrocyanide, as represented diagrammatically in figure 4a. The counter ions are hydrogen ions which form the diffuse outer portion of the double layer. Some of the hydrogen ions are held so strongly (adsorbed) by the attractive force of the inner layer that they are not detected by a hydrogen electrode, whereas others, because of a relatively higher kinetic energy, exert sufficient osmotic repulsive force against the attraction of the adsorbed ferrocyanide ions so that they are a part of the intermicellar solution and thus influence the hydrogen

electrode. These are represented in the diagram beyond the dotted line. On adding an electrolyte such as barium chloride to the sol, the divalent barium ions are attracted more strongly by the inner layer than the counter hydrogen ions, as shown diagrammatically in figure 4b, and the thickness of the double layer is reduced. At the same time, some adsorbed hydrogen ions are displaced and are detected in the intermicellar solution. This contraction of the double layer or compression of the outer layer resulting from stronger adsorption of barium ions than hydrogen ions under the prevailing relative concentrations, causes a lowering of the ζ -potential

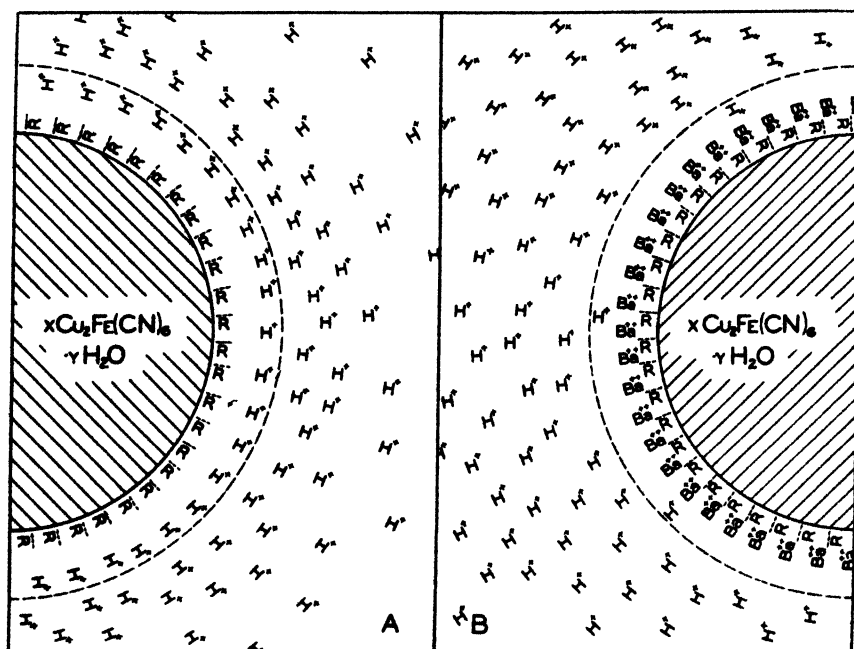


FIG. 4. Diagrammatic representation of the constitution of a particle of colloidal cupric ferrocyanoide before and after the addition of Ba^{++} .

on the particles; when this is reduced sufficiently, coagulation takes place. The displacement of adsorbed hydrogen ions by adsorbed barium ions is far from an equivalent displacement, since most of the adsorbed barium ions correspond to hydrogen ions which are in the intermicellar solution and so are measurable potentiometrically in the original sol. It is not at all surprising that in certain cases all the adsorbed hydrogen ions are displaced before sufficient barium ions are adsorbed to reduce the ζ -potential to the coagulation point.

Since most of the added barium ions are adsorbed at concentrations slightly above the coagulation value, it would follow that most if not all the

added barium ions are adsorbed *below* the coagulation value. Since the total barium adsorbed above the coagulation value is somewhat greater than the total hydrogen ions in the sol, it follows that, to a certain extent, both barium ions and chloride ions are adsorbed in equivalent amounts from the barium chloride solution. The observed phenomena are almost identical with those using the positive hydrous oxide sols of iron, aluminum, and chromium in which the counter ions are chloride ions, and the precipitating electrolyte is potassium sulfate (11). The behavior of strontium chloride is similar to that of barium chloride, whereas potassium chloride has a lower precipitating power, because potassium ions are less strongly adsorbed and displace hydrogen less strongly than the divalent ions at the same concentration.

From the above observations it is concluded that the action of electrolytes on cupric ferrocyanide sol is similar to that previously observed on five other sols. The lowering of the ζ -potential of the cupric ferrocyanide particles on the addition of electrolytes is due to the contraction of the double layer or, if preferred, to a compression of the outer layer resulting from adsorption of the added cations. At all concentrations the cation adsorption is much greater than the hydrogen-ion displacement, since most of the counter ions in the diffuse layer are in the intermicellar solution. The adsorption is for the most part an exchange adsorption, in which the cations carried down are in exchange with the counter hydrogen ions of the diffuse outer layer. The apparent difference in behavior between the sols investigated in this laboratory and the silver iodide sol studied by Verwey and Kruyt, is that in the former the potential reduction results from adsorption of precipitating ions, whereas in the latter, adsorption may not be essential for all the potential reduction. It is a matter of opinion whether the behavior of the six sols which we have studied should be regarded as special, whereas that of the silver iodide sol typifies the general behavior as claimed by Verwey and Kruyt, or whether the reverse is true.

SUMMARY

1. A study has been made of the adsorption of cations and of the displacement of hydrogen ions during the electrolyte coagulation of negative cupric ferrocyanide sol prepared by peptization of cupric ferrocyanide gel with hydroferrocyanic acid.

2. At concentrations both above and below the precipitation value, the adsorption of cations is much greater than the displacement of hydrogen ions, since most of the hydrogen ions, which constitute the diffuse outer portion of the double layer surrounding the particles, are in the intermicellar solution.

3. The adsorption of cations is largely an exchange adsorption, in which the cations carried down by the precipitated gel are in exchange with

the counter hydrogen ions of the diffuse outer portion of the double layer.

4. The lowering of the ζ -potential of the cupric ferrocyanide particles on the addition of electrolytes is due to the contraction of the double layer, or, if preferred, to a compression of the outer layer resulting from adsorption of the added cations.

5. The behavior of cupric ferrocyanide sol toward electrolytes is similar in essential respects to that of hydrous oxide sols, sulfur sol, and arsenic trisulfide sol investigated in this laboratory.

6. The apparent difference in behavior between the six sols studied by us and the silver iodide sol studied by Verwey and Kruyt, is that in the former the potential reduction results from adsorption of precipitating ions, whereas in the latter, adsorption may not be essential for all the potential reduction.

REFERENCES

- (1) FREUNDLICH, JOACHIMSON, AND ETTISCH: *Z. physik. Chem.* **141A**, 249 (1929).
- (2) KOLTHOFF AND TOMSICEK: *J. Phys. Chem.* **39**, 955 (1935).
- (3) MCBAIN AND McCLATCHIE: *J. Am. Chem. Soc.* **55**, 1315 (1933).
- (4) MÜLLER: *Kolloidchem. Beihefte* **26**, 257 (1928).
- (5) MÜLLER, WEGELIN, AND KELLERHOFF: *J. prakt. Chem.* [2] **86**, 82 (1912).
- (6) VERWEY AND KRUYT: *Z. physik. Chem.* **167A**, 137, 149, 312 (1933).
- (7) VERWEY: *Chem. Rev.* **16**, 363 (1935).
- (8) WEISER AND MIDDLETON: *J. Phys. Chem.* **24**, 30, 630 (1920).
- (9) WEISER: *J. Phys. Chem.* **34**, 335 (1930).
- (10) WEISER: *J. Phys. Chem.* **35**, 1 (1931).
- (11) WEISER: *J. Phys. Chem.* **35**, 1368 (1931).
- (12) WEISER AND GRAY: *J. Phys. Chem.* **36**, 2178 (1932).
- (13) WEISER AND GRAY: *J. Phys. Chem.* **36**, 2796 (1932).
- (14) WEISER AND GRAY: *J. Phys. Chem.* **39**, 1163 (1935).
- (15) WEISER AND MILLIGAN: *Trans. Faraday Soc.* **32**, 358 (1936).

ERRATUM

Vol. 40, p. 988: Reference 12 should read "HARKINS AND BROWN: J. Am. Chem. Soc. **41**, 499 (1919)."

THE ADSORPTION CONDENSER AND ELECTROMOTIVE FORCE¹

JOSEPH F. CHITTUM AND HERSCHEL HUNT

Department of Chemistry, Purdue University, West Lafayette, Indiana

Received June 11, 1936

The controversies concerning the origin of electromotive force have offered a great stimulus for the development of electrochemistry (14). The existence of a metal-surface work function in the surface of metals immersed in water is either denied or ignored by a number of electrochemists (18). Others, reasoning from the behavior of metals in the highest vacuum obtainable, consider that a condenser must exist with or without a chemical reaction at the surface. To date no important tool for the complete understanding of electrochemistry has been evolved from either the chemical-reaction or the contact-potential theory, although the latter has the advantage.

The pioneering work of Butler (3) pointed the way for development. Shortly after Butler's work the picture of a metal became much more complicated. The Sommerfeld (16) and Bloch (1) theories of metals gave a much clearer picture of the energy relationships at the metal surface. These theories divided the total metal-surface work function into two parts, the internal and the external work function. Gurney (9) modified the external work function by introducing a division termed the "interface" potential to account for the resultant condenser in the interface of a metal in a solution. The "interface" potential seemed absolutely new, but in reality Gurney merely used the concepts and language of molecular spectroscopy to describe the forces that cause the adsorption of ions on an electrode, and named the potential of the adsorption condenser the "interface" potential. He showed that the energy which produces the adsorption of ions can be represented as the difference between two electron energy levels,—the electron energy level of the metal and the electron energy level of the ion in solution. After he had proved the necessity for an increased adsorption of ions during the passage of current across a metal interface, he explained the overvoltage data of Bowden (2). Bowden adjusted his electrodes until their potentials were that of the equilibrium hydrogen or oxygen electrode at the start of the experiment.

¹ Presented at the Thirteenth Colloid Symposium, held at St. Louis, Missouri, June 11–13, 1936.

The hypothesis of ion adsorption on the surface of metals has been a very important part of a large number of theories of the phenomena of metal surfaces. Helmholtz (10) in 1879 suggested an ion adsorption condenser to explain a number of characteristics of metals, including electrokinetic potentials. His theory has been modified and extended by a large number of theorists, including Debye and Hückel (5), Gouy (8), Stern (17), and Freundlich (7). Langmuir pointed out that an ion adsorption condenser furnishes the only true potential of an electrode. The structure of the adsorption condenser is in dispute, but there is general agreement that the adsorbed layer must be mobile enough to participate in electrokinetic phenomena and it must be sensitive enough to the concentration of the ions in the solution so that its contribution to the electrode potential will be in accord with the thermodynamic equation of Nernst.

Our (4) recent experiments on the rapid motion of metals through solutions indicate that electrokinetic potentials at crystalline metal surfaces are produced by the disturbance of a layer of adsorbed colloidal particles. The rate of build up and decay of the potential is too slow for the phenomenon to be due to the behavior of simple ions (12). Metallic colloids have a characteristic effect on the potential. The chemical reaction theory is eliminated. In other experiments we (11) produced very large electrokinetic potentials at noble metal electrodes during overvoltage measurements at low current densities. It seems still more obvious that the latter are due to the disturbance of a layer of colloidal particles in the interface. If the very important principle of Butler and Gurney, that "the passage of a certain current across an electrode interface necessitates a certain overpotential," is to be accepted, any great disturbance of the overvoltage at low current densities by movement of the interface through the solution indicates (1) that a part of the hypothetical equilibrium condenser has been disturbed, and (2) that this part of the equilibrium potential is made up not of the ions of the solution whose concentration is established by the current, but of colloidal particles of hydrogen and metal.

In the experiments on overvoltage another very interesting phenomenon was observed. The metals copper, silver, gold, and platinum, when polarized cathodically in pure dilute aqueous sulfuric acid solutions at current densities of less than 10^{-5} ampere per square centimeter, showed electrode potentials in the platinum direction from the equilibrium hydrogen electrode. The solutions were very carefully freed from traces of oxygen by boiling and cooling in a stream of purified hydrogen; purified hydrogen was bubbled through the solution during the measurements. Previous cathodic polarization at high current strengths and moving the metal rapidly through the solution cause the potentials to go farther in the platinum direction. Long periods of polarization in an apparatus where the hydrogen gas could be collected proved that hydrogen was not liberated.

Weighing the cathodes before and after the individual experiments and spectroscopic analyses of the anodes showed that colloidal particles of metal carrying a negative charge were plated off of the cathodes.

Examples of the plating of metals off of cathodes are quite numerous in the experience of electroplaters; the phenomenon is most baffling in the light of the principles accepted at present. Kohlschütter (13) has ultra-photomicrographic evidence that there are colloidal particles in the electrode interface and claims that they play an important part in the electroplating process. Our experiments establish "the solution-of-the-negatively-charged-cathode-colloids" as the explanation of plating-off processes and indicate most clearly the need for a theory in which colloidal particles play a very important part.

The point from which we think the theory should start is indicated by the results of the recent experiments on electron diffraction from pure polished metal surfaces. Attempts to secure an indication of structure in a polished metal surface using electron methods always fail. The beam is diffused into broad lines. Since it is possible to get an indication of structure from natural crystal surfaces that are essentially plane, the results of the experiments on polished metals indicate quite definitely that such a surface is made up of particles of finely divided metal. Such a premise leads logically to the conclusion that finely divided particles are an intrinsic part of the metal surface, and that polishing a surface merely thickens the layer.

During the rest of this discussion we shall outline a theory of electrode potentials in which we consider a single electrode potential as being composed of the metal-surface work function and a colloidal adsorption condenser.

THE METAL

The conception of a metal which we shall use is essentially that originated by Sommerfeld and modified by Bloch. For some purposes all of the electrons of the metal atoms may be considered as being free to move from one end of a perfect lattice to the other without resistance. Electrical resistance is produced by a disturbance of this lattice. For the purposes of the quantum statistics, the electrons may be considered as bound in energy levels to which they are assigned according to the Pauli exclusion principle. The outermost electrons, the so-called valence electrons, behave like a very highly compressed or degenerate gas, obeying the Fermi-Dirac statistics. They are the only ones that can respond to an external electric field, make transitions to higher energy levels of the electron gas, change direction under influence of an electric field, and hence participate in the electronic conduction process.

These principles apply only as long as the perfect lattice exists. Local

irregularities, such as the surface of the perfect crystal, introduce new levels. For example, some space charge barrier must balance the maximum kinetic energy of the electrons, from 2 to 20 volts, so that the only effective electron barrier is the external work function. Such a space charge barrier might be formed by an impurity that, being stuck to the surface, becomes charged by induction and so affects the periodicity of the field near the boundary that the lower energy levels are damped out. The external metal-surface work functions, however, are measured when the possibility of impurities being present is at a minimum. At any rate it is not desirable to develop a theory of an ideal metal surface assuming the existence of an impurity. As has already been pointed out, there has accumulated an appreciable amount of direct and deductive evidence for the existence of a layer of finely divided metal in the metal surface. Therefore our theory assumes the adsorption on a pure metal surface of a layer

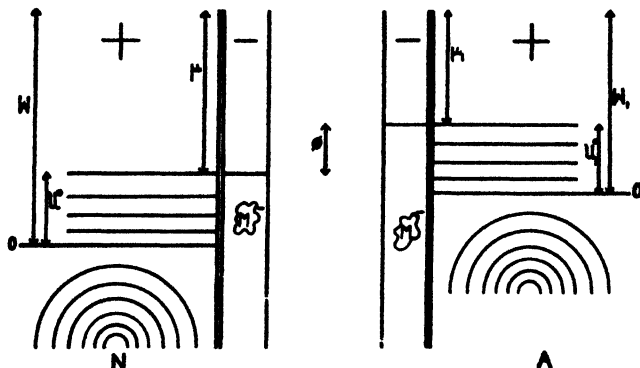


FIG. 1. The energy relations at the surface of a noble (*N*) and an active (*A*) metal in a vacuum

of finely divided metal particles that are charged with excess negative charges (electrons) sufficient to balance the maximum kinetic energy of the metal electrons.

The energy relations at the surface of a noble and an active metal in a vacuum are represented by *N* and *A*, respectively, in figure 1. *W* and *W*₁ are the total metal-surface work functions, or the potential barriers for an electron of zero kinetic energy; *μ* and *μ*₁ are the external metal-surface work functions, or the potential barriers for an electron of maximum kinetic energy; *U*⁰ and *U*₁⁰ are the maximum kinetic energies of the electrons at 0°K. *U*⁰ is given by the equation,

$$U^0 = \left(\frac{h^2}{2m} \right) \left(\frac{3n}{8\pi} \right)^{2/3} \quad (1)$$

where h is Planck's constant, m is the mass of the electron, and n is the number of electrons per unit volume. The energy distribution function expressing dn_w , the number of electrons per unit volume whose total kinetic energies lie between w and $w + dw$, is

$$dn_w = \frac{A w^{1/2} dw}{e^{-\frac{(U^0 - w)}{kT}} + 1} \quad (2)$$

It is possible to show from this distribution function that U^0 may be used as the approximate value of the maximum kinetic energy of the electrons at room temperature. The relatively enormous velocities of the electrons are counteracted at the metal surface by a layer of negatively charged metal particles, while the crystalline metal assumes a positive charge as a result of the particles being negatively charged (see figure 1). Any electron that gets inside of this layer will be accelerated enormously toward the crystalline metal, and an electron emerging from the metal surface with the maximum velocity will have its velocity reduced to zero by the time it reaches the particle layer. Therefore it is necessary to give the electron the additional energy, μ , in order that it may overcome the force due to the attraction of the electric image and the force due to the attraction of the electrostatic environment and escape.

THE SOLUTION

We shall consider the solution in which the metal is immersed from the energy level point of view in much the same way that Fowler (6) has. Positive ions and dissolved oxidizing agents are regarded as possessing empty electron energy levels. In the gas phase, positive ions have rather low energy levels (large ionization potentials), but when they dissolve in a polar solvent such as water, ions of the metals above hydrogen lose considerable energy so that their energy levels are raised, while ions of the metals below hydrogen gain energy so that their energy levels are lowered. When the positive ion is stable its empty energy level must be equal to or above any full electron energy level in the metal, such as the maximum kinetic energy level, or the full energy level of a negative ion. The energy level of a positive ion in solution can be raised, with respect to a metal energy level, by diluting the salt furnishing the positive ion or by giving the solution a negative charge with respect to the metal. The energy level of a positive ion in solution can be raised with respect to a negative ion only by dilution.

The negative ions and dissolved reducing agents are regarded as possessing full electron energy levels in the solution. The negative ions in the gas phase have energy levels that are not as low, on the energy scale, as

the energy levels of the positive ions. The two kinds of ions neutralize each other on collision. When the negative ions are dissolved in a polar solvent like water their energy level is lowered until both positive and negative ions exist as separate ionic species. It is necessary for the energy level of a negative ion to be lower than the metal energy level because the metal furnishes the electron supply. The energy level of the negative ion can be lowered with respect to a metal energy level by dilution, or by giving the solution a positive charge with respect to the metal. The energy level of a negative ion can be lowered with respect to a positive ion only by dilution.

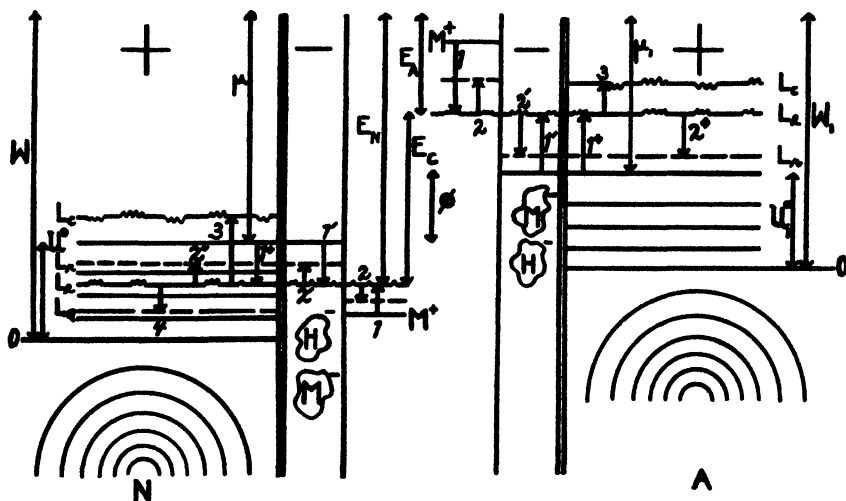


FIG. 2. The result of the raising of the energy level of the positive ions of an active (A) and of a noble (N) metal

If the electron energy level of an ion is occupied by an electron it is a full level; if it is not occupied it is an empty level. For any ion species that participates in the reactions at an electrode interface the full and the empty energy levels tend to be the same.

THE ELECTRODE

When a metal is placed in an aqueous solution of its salt the energy relations in the surface are changed. The colloidal particles become identified with the electrical surface of the solution, so that any charge on the colloidal particles is now the net charge on the solution. The instantaneous effect is the raising of the electron energy level of the solution ions in the surface of the layer, owing to the charge the colloid had in a vacuum. The result of the raising of the energy level of the positive ions of an active metal is

shown in figure 2(A) at M^+ . The empty positive ion level is higher than the metal energy level. The colloidal layer will have metal atoms on the surface of the particles that can be considered as solution ions possessing full energy levels. These full energy levels must lose electrons to the crystalline metal, producing a decrease in the negative charge on the solution, a decrease in the positive charge on the metal, and a positive ion in the solution. As a final result when equilibrium is reached the metal energy level is raised and the empty positive ion energy level is lowered until the two levels are the same. This situation is shown at L_e , figure 2(A).

The immediate result of the raising of the energy level of the ions of a noble metal is represented in figure 2(N) at M^+ . The empty energy level of the solution ion is below the energy level of the electrons in the metal. Electrons can flow from the metal into the ion level, producing a full positive ion level or a neutral metal atom that deposits on the crystalline metal. This process charges the solution more negatively and the crystalline metal more positively, so that the metal energy level is lowered while the energy level of the solution ion is raised until the two levels are the same and equilibrium is established. This latter situation is represented at L_e , figure 2(N).

When equilibrium is reached at an electrode the energy barrier for the electrons in the metal is changed from μ to $\mu - fV = fE$, where V is the interface potential for the electrode, $\mu = W - U^0$, the external metal-surface work function, E is the electrode potential, f is the charge on the electron, and fV is the energy of transformation 1', shown in figure 2. Any lack of definition of the energy levels is matched on the inside and outside of the metal. The current of electrons leaving the perfect lattice of the metal and neutralizing solution ions of the colloidal layer is given by the expression

$$i_1 = K_1(M^+)Te^{\frac{-(W_1 - U^0 - n f V)}{2 R T}} \quad (3)$$

where M^+ is the activity of the metal ions. The current of electrons, from the full energy levels in the colloidal layer, that flows into the metal leaving ions to be hydrated in the solution is given by the expression

$$i_2 = K_2(P)Te^{\frac{+(W_1 - U^0 - W_h - n f V)}{2 R T}} \quad (4)$$

where P is a constant characteristic of the metal and W_h is the energy of hydration of the ions. When the electrode is in equilibrium, the currents i_1 and i_2 are equal. Equating equations 3 and 4 gives

$$nFE = \frac{W_A}{2} + RT \ln \frac{K_1(M^+)}{K_2(P)} \quad (5)$$

or

$$E = E_0 + \frac{RT}{nF} \ln (M^+) \quad (6)$$

which is the thermodynamic equation of Nernst.

A cell made up of the two different types of electrodes such as those shown in figure 2 can be represented by a solution connection between the two interfaces. The electromotive force of the cell, measured on a potentiometer, would be $E_c = E_A - E_N$, or the difference between the energy levels of the solution ions in the colloidal layers of the two electrodes. The contribution of the metals to the electromotive force is the contact difference of potential, ϕ (figure 1). The contribution of the solution to the electromotive force is $EV - EV_1$.

ELECTROKINETIC POTENTIALS AT METAL SURFACES

The importance of the rôle played by the colloidal particles in supplying either empty or full energy levels (metal atoms) to the positive ions in solution is emphasized by a consideration of what happens when an electrode is moved rapidly through a solution. It is obvious that the large frictional and centrifugal forces will throw the particles out into the solution. This removal of the colloidal particles removes the source of full electron energy levels to a position where the tendency of the electrons to leak to the metal is reduced, and if the instantaneous energy level of the solution ions, M^+ , is any above or below the metal energy level in a vacuum the effective electrode potential changes.

Let us consider an active metal in pure water first. The removal of the colloidal particle makes it possible to set up only a false equilibrium. The positive ion level will return toward its instantaneous position, M^+ , and the metal energy level will return toward its position in vacuum, transformations 2, 2', and 2'' (figure 2). The solution gets a more negative charge in order to balance the kinetic energy of the metal electrons at L_+ , and the chemical reaction fills empty hydronium ion levels. The electrode potential of the metal changes in the platinum direction. If the above experiment on the electrokinetic potential of an active metal is repeated in solutions of its salts, the electrokinetic potential of the metal is not so large. The decrease in the electrokinetic potential is not dependent upon the increased activity of the salt in the solution alone, but also upon the effect of the colloidal particle in solution upon the energy levels of the ions. It is not very easy to predict the shape of the electrokinetic potential-concentration of electrolyte curve, so it will not be attempted here.

Violent motion of the noble metal in water wipes off the colloidal particles. The energy level of these particles is below the energy level of the hydronium ion, and since the negative charge on the solution is too great to balance the maximum kinetic energy of the metal electrons, electrons are forced into the metal. The energy level of the metal in vacuum tends to be restored and the electrode potential changes in the sodium direction, L_r . If the solution contains positive ions into which the electrons can flow, an added salt, then the potential of the electrode may change in the platinum direction.

The predictions that have been made concerning the electrokinetic potentials at metal surfaces, using the colloidal layer theory, are in very good agreement with the facts. The magnitude and sign of the electrokinetic potentials of metals in pure water are correct for improving the agreement between metal-surface work functions and molal electrode potentials.

THE HYDROGEN ELECTRODE

According to the general description given of an equilibrium electrode, the hydrogen electrode must be an electrode whose potential is dependent upon the energy level of the hydronium ions in solution. The hydronium ions in solution must have a supply of both empty and full energy levels, the hydronium ion level must be the same as the metal energy level, and the metal energy level must be in equilibrium with the hydrogen gas molecules when equilibrium is reached. The metal must supply a large amount of colloidal metal to adsorb the monatomic hydrogen. The colloidal layer must possess monatomic hydrogen or ions with full energy levels. The height of the full energy levels of the hydronium ions is determined by the partial pressure of the hydrogen gas. The base metal must not be capable of reacting with hydrogen ions. When these conditions are fulfilled the equilibrium processes that take place at a hydrogen electrode can be described exactly as those of the pure metals. Any increase in the height of the full level in the colloidal layer due to the neutralization of positive ions or increase in the hydrogen gas pressure causes a flow of electrons to the metal. These electrons arriving at the metal raise the energy level of the metal until the electrons flow back to an empty level of the colloidal layer, thereby reestablishing the original condition.

THE OXYGEN AND CHLORINE ELECTRODES

The contact-potential theory of electromotive force has been difficult for many chemists to accept, because it has not given a clear picture of an equilibrium oxidizing gas electrode such as the oxygen or chlorine electrodes. The colloidal adsorption theory eliminates this difficulty when it shows that the energy levels of the empty ion (monatomic gas) and the full ion are the same as the energy level of the metal. The energy level of the

metal must be largely established by the oxidation potential of the oxidizing gas, and the height of the level of the empty ion must be sensitive to changes in the partial pressure of the gas. The only difference between these electrodes and the ordinary metal electrodes is that the full energy level of the solution ion is represented by a negative ion, while the empty level is represented by a monatomic gas. In the case of oxygen and chlorine the potential at equilibrium is quite far in the positive direction.

The practical difficulty encountered in producing an equilibrium electrode for an oxidizing gas is due to the difficulty in finding a metal whose colloidal layer will produce ions with an empty energy level from the gas molecules. It is naturally easier to produce an equilibrium chlorine electrode than an equilibrium oxygen electrode, because in the first case the empty level that must be supplied is monatomic chlorine, while in the latter case the empty level is the free hydroxyl radical, whose energy level is below the energy level of monatomic oxygen, owing to hydration.

AN ELECTRODE CARRYING A CURRENT

In treating an electrode that carries a current we use the principle proved by Gurney. The probability of the passage of the excess electrons in the current direction (as a result of the quantum mechanical tunneling principle) must account for the current density. The equation for the net current across the interface is given by the equation

$$\pm i = K_1(M^+)T_e \frac{-(W_1 - U^0 - n F V)}{2 R T} - K_2(P)T_e \frac{-(W_2 - U^0 - W_A - n F V)}{2 R T} \quad (7)$$

which is a combination of equations 3 and 4. Excess electrons can pass in one direction only when a full electron energy level is higher on one side of the electrode interface than an empty level on the other, as we have emphasized before. The full energy levels are higher on the metal side at a cathode, L_c , and on the solution side at an anode, L_a .

When the positive solution ions are the ions of a noble metal, a slight increase in the negative potential of the electrode causes electrons to leak through the condenser and neutralize the metal ions in the colloidal layer (see L_c , figure 2 (A)). The metal atoms crystallize onto the perfect crystal. The increase in potential determines the current density according to equation 7. If the positive solution ions are hydronium ions or the ions of some active metal, the potential of the electrode must be raised until the energy level of the metal is above that of the other metal ions in the colloidal layer of the solution. While the potential is being raised the current across the interface is carried into the solution by the colloidal particles accepting more electrons and then leaving the interface, owing to the applied potential. After the energy level of the metal reaches that of the solution ions, the electrons fall into these empty levels and the metal plates

out of solution. If the solution ions are of two different species, the one whose empty energy level is exceeded first by the metal level is neutralized. When the two different species have the same energy level the two plate out together.

The active metals show the same type of behavior, except for the fact that the change in potential, produced by violent motion of the metal, is of the opposite sign. Consequently equation 7 can not be used to predict the shape of the current density-overvoltage curve when there is active gas evolution. On account of the well-known lack of smoothness of metal surfaces and on account of the fact that the surface smoothness is constantly changing, there is a theoretical reason for both the lack of definite meaning for and the lack of reproducibility of the current density-overvoltage curves for the deposition of electrolytic gases at high current strengths.

In the case of high current densities, rotation redistributes the colloidal metal on the crystalline surface as well as the lines of force, so that the overvoltage will always be sent in the platinum direction. In the case of oxygen overvoltage these same factors will naturally send the potential in the sodium direction.

SUMMARY

An explanation of overvoltage and electrokinetic potentials is offered. The origin of electromotive force is described as well as the mechanism for conduction processes at a metal-solution interface. The explanation is based upon a colloidal layer of metal on the crystalline metal surface.

REFERENCES

- (1) BLOCH: *Z. Physik* **52**, 555 (1928).
- (2) BOWDEN: *Proc. Roy. Soc. London* **120A**, 59 (1928); **125A**, 107 (1929).
- (3) BUTLER: *Trans. Faraday Soc.* **19**, 729 (1924).
- (4) CHITTUM AND HUNT: *Trans. Electrochem. Soc.*, (1937).
- (5) DEBYE AND HÜCKEL: *Physik. Z.* **25**, 49 (1924).
- (6) FOWLER: *Trans. Faraday Soc.* **28**, 368 (1932).
- (7) FREUNDLICH: *Colloid and Capillary Chemistry*. Dutton and Co., New York (1926).
- (8) GOUY: *Ann. phys.* [9] **7**, 129 (1917).
- (9) GURNEY: *Proc. Roy. Soc. London* **134A**, 137 (1931).
- (10) HELMHOLTZ: *Ann. phys.* [2] **7**, 337 (1879).
- (11) HUNT AND CHITTUM: *J. Phys. Chem.* **41**, (1937).
- (12) KOENIG: *J. Phys. Chem.* **39**, 455 (1935).
- (13) KOHLSCHÜTTER: *Trans. Electrochem. Soc.* **45**, 229 (1924).
- (14) LANGMUIR: *Trans. Electrochem. Soc.* **29**, 125 (1916).
- (15) RANDALL AND ROOKSBY: *Nature* **129**, 280 (1932).
- (16) SOMMERFELD: *Z. Physik* **47**, 1 (1928).
- (17) STERN: *Z. Elektrochem.* **30**, 508 (1924).
- (18) DE KAY THOMPSON: *Trans. Electrochem. Soc.* **63**, 161 (1933).

THE DIRECT EXAMINATION OF SOLS BY X-RAY DIFFRACTION METHODS¹

W. O. MILLIGAN AND HARRY B. WEISER

Department of Chemistry, The Rice Institute, Houston, Texas

Received June 11, 1936

The application of x-ray diffraction methods to the determination of the constitution of sols has usually been indirect. X-ray diffraction studies have been made on the dry powder or moist gel obtained from the sol by precipitation with electrolytes, ultrafiltration, or centrifuging. In previous papers (10, 12) it was shown that, in general, the moist gels obtained by ultrafiltration of sols give the same x-radiograms as the dry powder. Thus with alumina, stannic oxide, and indium hydroxide sols, the moist gels obtained by ultrafiltration give the pattern of $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, SnO_2 , and $\text{In}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ or $\text{In}(\text{OH})_3$, respectively. Although it is often assumed that the sol particles have the same constitution in the sol state as in the moist precipitate, the direct examination of sols by x-ray diffraction methods should prove whether or not this is the case.

Very little work has been published on the direct examination of sols by x-ray methods. Kraemer (5) in discussing the application of x-ray methods to colloids states, "this technic [x-ray method] yields no results for the surface of particles, nor is it effective (as yet) in dealing with colloidal solutions." Björnsthål (3) examined gold and silver sols by allowing them to flow through a tube of gold-beaters' skin centered in the camera and obtained patterns which agreed with those for metallic gold and silver, respectively. The important investigations of Böhm and Niclassen (1) on the gels of various hydrous and hydrated oxides and hydroxides, has been supposed by some people to include investigations of sols in the sol state. Professor Böhm in a private communication states, "Die Aufnahmen für die Arbeit in der Z. f. anorganische Chemie, 132, 1 (1924) wurden, wie Sie richtig vermuten, an den meist feuchten *Rückständen* von Solen nach dem Koagulieren oder Eindampfen (so beim Crum'schen Sol) gemacht." Böhm and Ganter (2) examined *liquid sols* by flowing aged ferric oxide and vanadium pentoxide sols through a Mark tube and observed some indication of orientation of the needle-like particles. Our first work (10, 12) on the direct examination of a sol was

¹ Presented at the Thirteenth Colloid Symposium, held at St. Louis, Missouri, June 11-13, 1936.

carried out on a thixotropic stannic oxide sol, which gave the pattern of stannic oxide. More recently Heller, Kratky, and Nowotny (4) examined various ferric oxide sols in thin glass capillary tubes. These investigators obtained the patterns of FeOCl , $\beta\text{-FeOOH}$ (11), and $\gamma\text{-FeOOH}$, only; no indication of the formation of complexes was observed.

In this paper will be given the results of an x-ray study of a number of representative sols with the object of obtaining direct evidence concerning the constitution of the colloidal particles.

EXPERIMENTAL

The chief difficulties in the direct examination of sols are (a) the relatively low concentration of the dispersed phase, (b) the scattering of x-rays

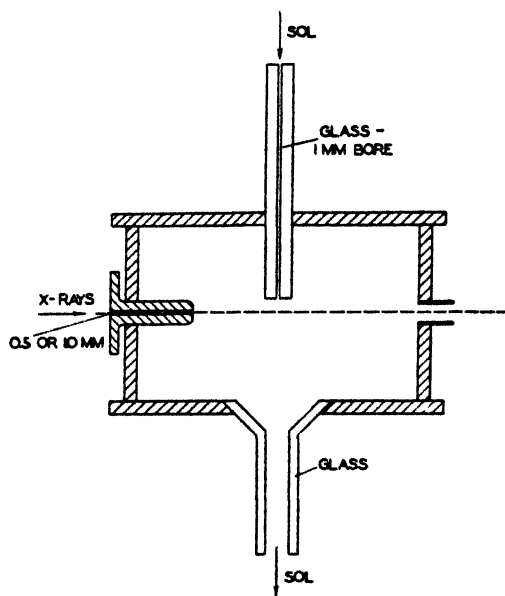


FIG. 1. X-ray diffraction camera for the direct examination of sols

by the water in the samples, and (c) the possibility of coagulation of the sol by the x-rays. The first and second difficulties may be obviated by using fairly concentrated sols; and the third by flowing the sols through the camera. Some objections may be raised to flowing the sol through a tube of any kind. For this reason, in most cases the sol was allowed to flow in an uninclosed column, in the same way that Debye originally examined liquids.

THE CAMERA

A Debye-Scherrer type of camera was employed, a diagram of which is shown in figure 1. The sol (or liquid) was allowed to flow into the capillary

tube. By maintaining a suitable head the rate of flow was adjusted so that a smooth, uninclosed column was obtained. In some cases a thin Mark tube was inserted in the capillary tube, giving a column of sol inclosed in glass. The scattering from the Mark tube is so small that it causes little or no difficulty. A possible objection to the use of the Mark tube is that solid particles might deposit on the walls and give the x-radiogram. However, there was no indication of this. A blank x-radiogram, obtained for a used but unwashed Mark tube as a sample, gave the same result as a new Mark tube. Furthermore, the same patterns were obtained using the inclosed and the uninclosed column of sol.

PREPARATION OF SOLS

Ferric oxide sol. A hydrous ferric oxide sol was prepared by the addition of a slight excess of ammonium hydroxide to a solution of ferric chloride. The resulting gel was washed rapidly by decantation until almost free from chloride, and a few drops of hydrochloric acid were added. Peptization and aging were brought about by warming for several hours at 60–65°C., while stirring vigorously with a mechanical stirrer. It has been shown (9) that the freshly precipitated hydrous ferric oxide gives no x-ray diffraction lines or bands, but that the material aged as described above gives the α -Fe₂O₃ pattern. This sol contained about 90 g. of ferric oxide per liter of sol.

Alumina sols. The two alumina sols examined were made by methods already described in detail (10). Sol I was prepared according to the method of Thomas (7) by peptization with hydrochloric acid. Sol II was prepared by the peptization of precipitated alumina with hydrochloric acid. The gels from these sols gave the γ -Al₂O₃·H₂O pattern (10, 12). Alumina sol I, which contained 11.0 g. of alumina per liter originally, was concentrated by evaporation to 55.0 g. of alumina per liter. Alumina sol II was concentrated by evaporation to 41.2 g. of alumina per liter.

Stannic oxide sol. The method of preparation of this Zsigmondy stannic oxide sol has already been described (10, 12). The concentration of the sol was 33.4 g. of stannic oxide per liter.

Indium hydroxide sol. A hydrous indium hydroxide gel was prepared by the interaction of a slight excess of indium chloride solution and a solution of ammonium hydroxide. The gel was washed by centrifuging until peptization began, after which a few drops of hydrochloric acid were added. The sol contains 22.1 g. of indium oxide (In₂O₃) per liter.

Beta ferric oxide monohydrate sol. The gel formed by the interaction of solutions of ferric chloride and ammonium carbonate was re-peptized with an excess of ferric chloride. The sol was purified by dialysis in the cold for three months, and was concentrated by boiling on a hot plate. It would be expected (9) that β -FeOOH would form under these conditions,

since this material results from the slow hydrolysis of ferric chloride solution. But since the sol is dark red, and β -FeOOH is yellow, the dispersed particles must not be all β -FeOOH. The sol contains 89.6 g. of ferric oxide per liter.

Titanium dioxide sol. This sol was prepared by the slow hydrolysis of titanium tetrachloride solution. A slightly acid solution of the salt was hydrolyzed by heating to boiling; the resulting gel of hydrous titanium dioxide was centrifuged to remove excess acid, and reprecipitated by suspending in water to which a few drops of hydrochloric acid were added. The sol contained 30.8 g. of titanium dioxide per liter. From the method of preparation, one would expect (8) the particles to consist of the rutile modification of the dioxide.²



FIG. 2. X-ray diffraction pattern for a hydrous ferric oxide sol (α -Fe₂O₃)

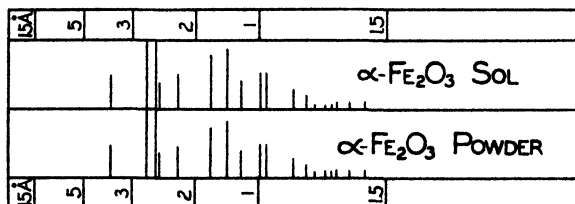


FIG. 3. X-ray diffraction patterns

Silver sol. The silver sol used was a commercial protected silver sol ("Argyrol") containing approximately 40 per cent silver.

Silver iodide sol. A silver iodide sol was prepared by mixing solutions of silver nitrate and hydriodic acid of such concentration that the resulting sol contained 80 millimoles silver iodide and 8 millimoles hydriodic acid per liter. The sol concentration was therefore 18.7 g. of silver iodide per liter.

X-RAY EXAMINATION

A hydrous ferric oxide sol was prepared and examined first in February 1934. The sol was not examined in the camera described in this paper, but

² Investigations which will be reported later are in progress on the preparation of gels of the rutile modification of titanium dioxide.

was flowed through a "nonex" glass tube in the General Electric diffraction apparatus, using Mo K_α radiation. The pattern obtained after ninety-six hours exposure is reproduced in figure 2. The results compared with



FIG. 5. X-ray diffraction patterns. A, H_2O ; B, $\gamma-Al_2O_3 \cdot H_2O$; E, SnO_2 ; G, $In(OH)_3$; K, $\beta-FeOOH$; K, TiO_2 (rutile); M, Ag; O, AgI.

$\alpha-Fe_2O_3$ powder are shown diagrammatically in figure 3. The pattern obtained with the sol is identical with that from crystals of $\alpha-Fe_2O_3$.

The other sols described above were examined in the special camera shown in figure 1, using a Philips cross-focus tube with Cu K_α radiation

(nickel foil filter). The exposure time was 30 minutes in all cases reported. While working with the ferric oxide sols a filter of aluminum foil was placed between the sample and the film to prevent fogging of the film by fluorescent x-radiation from the iron. For purposes of comparison, the pattern of distilled water was also obtained. To identify the patterns from the sols, x-radiograms were made from the corresponding powders, using the same camera. This was done by placing the solid in a Mark tube attached to the capillary tube in the camera. The results obtained from pure water, the various sols, and the various solid materials are given in chart form in figure 4. Reproductions of some of the negatives are given in figures 5. Alumina sol I containing 11.0 g. of alumina per liter (not included in figures 4 and 5) gave the pattern of $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$.

DISCUSSION OF RESULTS

From inspection of figures 4 and 5 it is apparent that in every case the sol pattern is a composite of the patterns from pure water and the material making up the sol particles. Thus in the case of the weak indium hydroxide sol the water bands are relatively intense, whereas in the case of the strong silver sol the water bands are hardly visible.

Only a slight indication of fibering in the pattern of the $\alpha\text{-Fe}_2\text{O}_3$ sol was observed. This sol was probably not aged as long as the one examined by Böhm and Ganter (6), who reported definite indications of orientation.

As pointed out under the method of preparation, the $\beta\text{-FeOOH}$ sol is red in color, whereas pure $\beta\text{-FeOOH}$ is definitely yellow. The results indicate that the sol consists of two portions: (a) yellow $\beta\text{-FeOOH}$ particles which give the lines in the x-radiogram, and (b) dark red particles of $\alpha\text{-Fe}_2\text{O}_3$ which are too fine to give a definite x-ray pattern (9). This conclusion is supported by an earlier observation (9) of the slow settling out of some $\beta\text{-FeOOH}$ particles during the aging of dark red sols.

The results confirm the previous conclusions of the authors (10, 12) based on the examination of moist gels, namely, that typical hydrosols of oxides, elements, or inorganic salts consist essentially of aggregates of minute crystals of the respective hydrous oxides or simple hydrates, simple elements, or simple salts. There is no indication of the presence in the sols of complexes such as postulated by Pauli (6), Thomas (7), and others.

SUMMARY

The following is a brief summary of the results and conclusions reported in this paper:

1. For the first time, a number of representative hydrosols have been examined directly by x-ray diffraction methods, taking precautions so that the resulting x-radiograms are for the actual sol particles.

2. A Debye-Scherrer type of camera has been designed especially for the direct examination of a completely uninclosed, flowing column of sol.

3. Alumina sols prepared (a) by the action of amalgamated alumina on water, and (b) by the peptization of precipitated alumina gave the pattern of $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$.

4. Ferric oxide sols were found to consist of particles of $\alpha\text{-Fe}_2\text{O}_3$ or $\beta\text{-FeOOH}$, depending on the method of preparation.

5. A stannic oxide sol (Zsigmondy), a protected silver sol ("Argyrol"), an indium hydroxide sol, a negative silver iodide sol, and a titanium dioxide sol gave respectively the patterns of SnO_2 (cassiterite), metallic silver, $\text{In}(\text{OH})_3$, AgI , and TiO_2 (rutile).

6. It is concluded, in agreement with previous x-ray studies on moist gels, that the common inorganic hydrosols consist in general of particles of simple oxides or simple hydrates, elements, or salts, and not of complexes as postulated by some investigators.

REFERENCES

- (1) BÖHM AND NICLASSEN: *Z. anorg. allgem. Chem.* **132**, 1 (1924).
- (2) BÖHM AND GANTER: Unpublished results reported in a private communication to the authors.
- (3) BJÖRNSTÅHL: Dissertation, Uppsala, 1924.
- (4) HELLER, KRATKY, AND NOWOTNY: *Compt. rend.* **202**, 1171 (1936).
- (5) KREAMER: in *Taylor's Treatise on Physical Chemistry*, Vol. II, p. 1611. D. Van Nostrand Co., New York (1931).
- (6) PAULI AND VALKO: *Elektrochemie der Kolloide*. Julius Springer, Vienna (1929).
- (7) THOMAS AND COWORKERS: *J. Phys. Chem.* **35**, 27 (1931); *J. Am. Chem. Soc.* **54**, 841 (1932); **56**, 794 (1934); **57**, 44 (1935).
- (8) WEISER AND MILLIGAN: *J. Phys. Chem.* **38**, 513 (1934).
- (9) WEISER AND MILLIGAN: *J. Phys. Chem.* **39**, 25 (1935).
- (10) WEISER AND MILLIGAN: *J. Phys. Chem.* **40**, 1 (1936).
- (11) WEISER AND MILLIGAN: *J. Am. Chem. Soc.* **57**, 238 (1935).
- (12) WEISER AND MILLIGAN: *Trans. Faraday Soc.* **32**, 358 (1936).

THE POLYMERIC CHARACTER OF BITUMINOUS COAL¹

H. C. HOWARD

Coal Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pennsylvania

Received June 11, 1936

The bituminous coals occupy an intermediate position in what has been called (15) the "coal band" (figure 1). Such organic substances as lignin and humic acids lie at one end of this band, and anthracite coal and graphite at the other. Whether lignin or cellulose is looked upon as the essential progenitor of bituminous coals, it appears that in the coalification process the simple linear polymeric structure, which is generally accepted for cellulose and which has been proposed (11) for lignin, is modified in the sense of the formation of a tridimensional polymer by linkages between the linear units. Whatever the mechanism, there is no doubt that the process is characterized by increasing enrichment in ring structures (6). The higher the rank of the coal, the more complete is the condensation to such structures, until graphite, the limiting member of the series, is reached. The establishment of a building unit in such a polymer obviously presents great difficulties, and we can perhaps never obtain as satisfactory a picture for the structure of such a substance as we have for cellulose and the polymeric esters, lactones, and anhydrides.

The essentially "chemical" character of polymerization has been emphasized in recent years (7), and in those cases where the energetics of the process have been investigated, the reactions have been shown to be exothermic; hence, one would expect elevated temperatures to displace the equilibrium toward depolymerization. Many such cases have long been known among the addition polymers such as styrene and rubber, and more recently the ready thermal reversibility of such purely condensation types as the polymeric lactones and anhydrides has also been pointed out (8).

A typical bituminous coal from the Pittsburgh seam contains carbon, hydrogen, and oxygen in approximately the same ratio as coumarone, C_8H_6O , which has a normal boiling point of 170°C .; the coal contains somewhat less oxygen and more hydrogen and such polar groups as hydroxyl and carboxyl are present, if at all, in very small amounts. Thus on the basis of composition alone, one would expect bituminous coal to distill completely at moderate temperatures. Its low volatility is ob-

¹ Presented before the Thirteenth Colloid Symposium, held at St. Louis, Missouri, June 11-13, 1936.

viously due to high molecular weight, but thermal decomposition would be expected to give some clue to the nature of the building units as it has in the case of other high molecular weight substances. That the ordinary distillation processes do not, appears to be due to the fact that in coal the primary unit itself has a very low vapor pressure. Hence in pyrolysis the rate of decomposition of this primary unit into secondary products, some of greater molecular weight (coke) and some of less (gaseous and liquid hydrocarbons and low-boiling phenolic bodies), is faster than its rate of

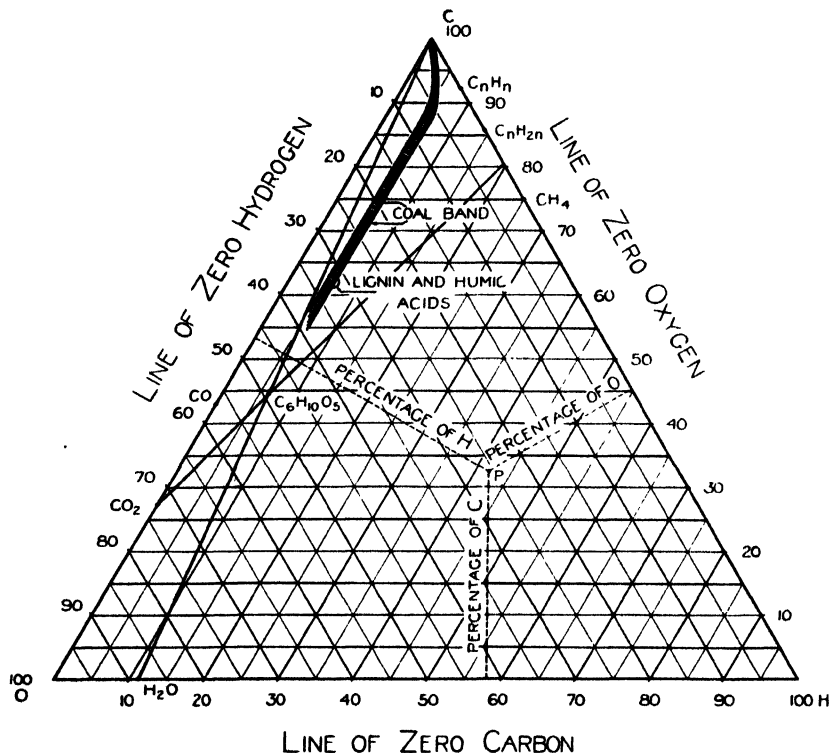


FIG. 1. The "coal band" and some typical carbon, hydrogen, and oxygen compounds evaporation. Certain methods of degradation, some purely thermal in character and others combining thermal and chemical effects, which yield significant information as to the nature of the building units in bituminous coal, have, however, been developed. These are (1) pyrolysis in the molecular still, (2) thermal decomposition in solvents at elevated temperatures, (3) hydrogenation, and (4) mild oxidation.

PYROLYSIS IN THE MOLECULAR STILL

When a bituminous coal is heated to 500–550°C. at pressures of 1 micron or less in a molecular still, where the distance between evaporating and

condensing surfaces is very much less than the mean free path of the evaporating molecules, and where the possibility of collision with surfaces hotter than the evaporating surface is eliminated, secondary thermal decomposition is largely avoided (13). The condensate obtained under these conditions contains, along with the usual liquid hydrocarbons and phenolic substances, appreciable amounts of brown, amorphous solids, neutral in character and readily soluble in such polar aromatic solvents as phenol, but almost completely insoluble in petroleum ether or ethyl ether. These substances have been designated "bitumens" by coal investigators. They can not be redistilled, even in the molecular still, without some decomposition, yielding gaseous and liquid hydrocarbons, phenolic bodies, bitumens, and a coke residue. The point of view that these neutral, ether-insoluble substances, the bitumens, constitute an important primary

TABLE I
Composition of condensates from atmospheric and vacuum distillations
Temperature, 525°C.

	ATMOSPHERIC	VACUUM	
	20-40 Mesh coal	20-40 Mesh coal	μ -Coal*
	per cent	per cent	per cent
Neutral			
Ether-insoluble (bitumens)	2 78	7 11	17 10
Ether-soluble	7 51	8 61	8 20
Phenolic and acidic	2 45	2 56	1 37
Basic	0 40	0 20	0 16
Water and loss	3 98	2 32	1 50
Total	17.12	20.80	28 33

* Prepared by grinding in a Szegvari pebble mill; particle size less than 2μ .

thermal degradation product of bituminous coal, is supported by the experimental facts that in the thermal decomposition of a given coal a reduction in pressure, an increase in heating rate, and a decrease in particle size of the coal all tend to increase the yield of bitumens. The effects of reduction in pressure and the use of coal ground to particles less than 2μ , designated μ -coal, are illustrated by the data of table 1. The increase in the amount of bitumen recovered in the condensate when the μ -coal was employed is very striking and shows that in a 20- to 40-mesh coal particle considerable secondary decomposition takes place before the evaporating substances can escape. Since phenolic bodies have been shown (14) to be secondary decomposition products of the bitumens, the decreased yield of the former with increased recovery of the latter is to be anticipated.

THERMAL DECOMPOSITION IN SOLVENTS

That resinous or bituminous substances could be extracted by solvents from bituminous coals at a temperature much below that at which they could be recovered by distillation has been known for many years. The early experimenters, working at low temperatures and recovering a few per cent of material, regarded the process as a simple solvent extraction, and considered the materials extracted to have been present as bodies which were of significantly different chemical constitution from, and hence much more soluble than, the bulk of the coal substance. With the development of pressure extractors and the use of new solvents (17) and of temperatures ranging from 250° to 350°C., the yield of "extract" rose as high as 80 per cent, thus showing that products at present not distinguishable from the resins and bitumens of the early investigators could be formed by thermal decomposition of the bulk of the coal substance. The point of view that solvent extraction at elevated temperatures should be looked upon as a mild thermal decomposition has been emphasized by Lowry (15); Peters and Cremer (16) point out that the small variation in chemical composition between extract and residue can not account for their marked physical differences, and hence one must assume that polymerization is involved. A recent study (3) of extract and residue from a bituminous coal from the Pittsburgh seam has shown that insofar as present knowledge permits these substances to be characterized, there is little difference between extract and residue other than in molecular weight, and that the extract can properly be considered a primary building unit in the coal polymer, depolymerization having been effected by the elevated temperature and the action of the solvent.

To what extent the degradation of coal by solvents at elevated temperatures involves the formation of colloidal dispersions rather than molecular solutions is not certain. Dark-field examination of these solutions at room temperature reveals colloid particles. The extracts, however, contain very little inorganic residue and it seems probable, if the phenomenon were chiefly peptization, that the peptized material would be of ash content similar to the coal. It appears more likely that the substances extracted are molecularly dispersed at the temperatures of the extraction process and associate or polymerize to the colloid units on cooling. Also, as will be seen later, all these products formed by solvent action at elevated temperatures give freezing-point depressions in phenolic solvents which correspond to molecular units of moderate size.

The yields of soluble products recovered by thermal decomposition of a bituminous coal from the Pittsburgh seam in benzene (1), phenol, and tetralin (2) at temperatures of 250–350°C. are shown in table 2. The much greater effectiveness of this type of degradation as compared with vacuum distillation is strikingly illustrated, as is also the specific action of

such a polar solvent as phenol, with which, at corresponding temperatures, a fivefold yield of soluble products over that with the non-polar benzene is obtained. Unfortunately attack by this method at still higher temperatures is limited by the thermal instability of the solvents themselves.

MILD HYDROGENATION

The effectiveness of mild hydrogenation in the primary breakdown of bituminous coal was demonstrated by F. Fischer, Peters, and Cremer (9), who found that by prolonged reaction at temperatures as low as 260°C., a German bituminous coal, ground to a particle size of less than 2 μ , yielded 85 per cent of material soluble in hot benzene. It is significant that these investigators designated the products recovered by this mild hydrogenation as "pseudo-bitumens."

TABLE 2
Decomposition in solvents at elevated temperatures

SOLVENT	TEMPERATURE	TIME	COMPOSITION OF EXTRACTS				
			Neutral		Phenolic and acidic	Basic	Total
			Ether-insoluble	Ether-soluble			
	°C	hours	per cent	per cent	per cent	per cent	per cent
Benzene	260	44	10 26	4 93	0 16	0 10	15 45
Tetralin	250	136	20 0	12 90	0 71	0 17	33 8
	300	126	12 3	4 34	0 32	0 15	17 0
	350	108	20 2	9 65	0 74	0 18	30 8
			52 5	26 89	1 77	0 50	81 6
Phenol	250	44	57 6	7 0	0 80	0 13	66 7

Work with a coal from the Pittsburgh seam has led to similar results, but a higher temperature, 350–400°C., has been found necessary. Under these conditions approximately 80 per cent of the American coal can be recovered in the form of high-boiling oils and bitumens.

MILD OXIDATION

When a bituminous coal is refluxed with dilute nitric acid, e.g., 1 *N*, it is rapidly converted to organic acids, some of which are of low enough molecular weight to be soluble in water or dilute acid, and others, the so-called regenerated humic acids, which are soluble in or peptized by alkali, but precipitate on acidification. The humic acids formed in this way usually represent not less than 60 per cent of the carbon of the original coal,

although this is a function of the period of oxidation, since these acids are the primary oxidation product and the water-soluble acids of lower molecular weight are secondary products (21). The rate of formation of both types of acids is a function of the rank of the bituminous coal, lower rank coals reacting with greater velocity.

The humic acids obtained by oxidation of bituminous coal dry to brownish-black or jet-black scales. They do not melt and on pyrolysis yield only low molecular weight volatile products, carbon dioxide, and water, and a carbonaceous residue. They form brown solutions with dilute alkalies, in which dark-field examination discloses many colloid particles. Their aqueous alkaline solutions diffuse only partially through parchment.

The alkali humates formed from coal show certain analogies to soaps: both form colloidal aggregates in aqueous solution; both are molecularly dispersed in solvents of the type ROH, where R is aliphatic in the case of

TABLE 3
Ultimate composition of bitumens and original coal

SOURCE	CARBON	HYDROGEN	OXYGEN	NITROGEN	SULFUR	ASH
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Molecular still, 525°C.	81 15	5 69	11 56	1 16	0 44	0 0
Pressure extraction:						
Benzene, 250°C.	84 70	6 32	5 71	1 59	0 68	1 08
Tetralin, 300°C.	82 21	5 06	10 00	1 16	0.43	1 14
Phenol, 250°C.	81 15	4 88	9 32	1 52	0.89	2 24
Hydrogenation*	85 25	7 27	4.88	1 88	0 42	0 30
Original coal	78 27	5 19	5 53	1 63	0 98	8 39
Ash-free	85 50	5 66	6 03	1 78	1 03	

* Hydrogenation of the residue from a benzene extraction at 250°C.

soaps and aromatic in the case of the humates; both are dispersing agents in aqueous solution; and both furnish aqueous solutions of high viscosity, although this is much less marked in the case of the humates because of plate-shaped rather than thread-like particles.

COMPOSITION OF THE BITUMENS AND THE HUMIC ACIDS

Ultimate compositions of bitumens obtained by different methods of degradation are shown in table 3. All contain, along with carbon and hydrogen, significant amounts of oxygen and small quantities of nitrogen and sulfur. Group tests indicate the absence of carboxyl, ester, carbonyl, or alkoxyl groups. Determinations of hydroxyl oxygen have given variable results depending upon the sample of bitumen employed and the method of methylation. Usually not more than half of the oxygen can, however, be accounted for as hydroxyl groups, and the balance must be

assumed to be in ether linkages or heterocycles. Hydrogenation at 425°C. of bitumens obtained by benzene pressure extraction, followed by dehydrogenation to aromatics and isolation of the crystalline picrates of the aromatics has resulted in evidence for the presence of condensed cyclic structures as large as four or five rings (4). Drastic oxidation of coal bitumens is reported (5) to result in high yields of benzene polycarboxylic acids. There thus appears little doubt that the nucleus of these bitumens consists of condensed C₆ ring structures with occasional heterocyclic rings containing oxygen, nitrogen, or sulfur.

The ultimate compositions and equivalent weights of humic acids prepared by mild oxidation of: (1) the whole coal, (2) bitumens extracted by heating with benzene at 250°C., and (3) the insoluble residue from the benzene extraction are shown in table 4. Carboxyl and hydroxyl groups can be determined by methylation; the latter are present in smaller amounts than reported for "humic acids" from other sources. There is

TABLE 4
Ultimate composition and equivalent weights of humic acids

SOURCE	CARBON	HYDRO- GEN	OXYGEN	NITRO- GEN	SULFUR	ASH	EQUIVA- LENT WEIGHT
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	
Original coal	61 46	3 21	30 4	3 36	0 65	1 1	240
Bitumen*	57 17	3 71	34 7	3 09	0 34	0 9	192
Residue†	60 17	3 89	31 4	3 04	0 55	1 0	244

* By oxidation of soluble material from benzene pressure treatment at 250°C

† By oxidation of insoluble residue from benzene pressure treatment at 250°C.

also evidence for the presence of isonitroso groups, but not more than one-half to two-thirds of the total oxygen can be accounted for in all functional groups together, indicating the presence of ether or heterocyclic oxygen. Little information is available as to the nature of the nucleus of these humic acids. Hydrogenation of the alkali humates by heating with sodium formate (10) at 360°C. results in simultaneous decarboxylation and conversion of the nucleus to high-boiling oils and bitumens. The latter are not distinguishable from bitumens obtained by degradation of the original coal.

MOLECULAR WEIGHT MEASUREMENTS

These preparations of primary degradation products of coal are, of course, not homogeneous. Determinations of average values of molecular weight have, however, led to interesting results. As has been pointed out, the bitumens are readily soluble in polar aromatic solvents such as phenol and catechol, and much less soluble in aromatic non-polar types such as

benzene and diphenyl. Only two solvents suitable for cryoscopic measurements on the regenerated humic acids have been found, namely, catechol (20) and *p*-nitrophenol.

The results of cryoscopic molecular-weight determinations on bitumens and regenerated humic acids, prepared in a number of ways from a coal from the Pittsburgh seam, are shown in table 5.

The significant feature of these data is the low and relatively constant values obtained in the solvents, catechol and *p*-nitrophenol. Considering the different methods of degradation employed, the relative constancy of these values argues strongly for the presence in this bituminous coal of

TABLE 5
Molecular weights of bitumens and humic acids

SOLUTE	SOLVENT					
	Catechol	<i>p</i> -Nitrophenol	<i>p</i> -Bromophenol	Tri-bromophenol	Pyrene	Di-phenyl
Bitumen from:						
Molecular still	250	220	320	360	(a)	(a)
Benzene extract	285		550	650		>1000
Tetralin extract	335		540			
Phenol extract	360		440			
Hydrogenation of residue ^(b)	320	320	550		960	>1000
Hydrogenation of humic acids ^(c) . .	260			510		>1000
Humic acid from:						
Original coal	235	230				
Bitumen ^(d)	215					
Residue ^(e)	240	280				

(a) Incompletely soluble. (b) Insoluble residue from benzene pressure extraction, hydrogenated at 350–400°. (c) Humic acids from original coal, hydrogenated at 350–400°. (d) Bitumen from benzene pressure extract. (e) Residue from benzene pressure extract.

some fundamental unit of the order of magnitude indicated. Wherever solubility permitted, measurements were made in several solvents. In such cases a rough correlation was observed between dipole moment of the solvent and apparent molecular weight, solvents of higher moment giving lower molecular weights. The differences noted between different solvents are much greater than has been found for known cases of molecular association. Two explanations appear possible to the writer: (1) association to colloid particles in the non-polar solvents or (2) actual degradation of a polymer by the polar solvents.

Such physical properties as vapor pressure and solubility indicate that both bitumens and regenerated humic acids are bodies of high molecular weight. It is known, however, that polar groups in certain positions

reduce volatility to a surprising degree. *p*-Hydroxybenzoic acid, for example, of molecular weight 138, is stated (19) to have a vapor pressure of 0.3 micron at 100°C., a value a thousandfold less than that for the *o*-hydroxy acid, salicylic acid. Further, while an average molecular weight of 300 appears low, an aromatic hydrocarbon of seven closely condensed rings has a molecular weight of only 302, and it should be noted that the molecular weight of the largest condensed aromatic structures which have been actually isolated from coal or pitch is smaller than this. It is also of interest that Fuchs (12), in picturing a hypothetical humic acid molecule, suggests a structure containing five condensed rings as the building unit, while Schrauth's (18) building element contains four six-membered and three five-membered condensed rings.

The presentation of the picture of bituminous coal as a polymer, built up of units of moderate molecular weight, naturally arouses the question as to how these units are in turn held together to form the high molecular weight body we know as coal. Unfortunately, very little can be said on this point at the present time. Considering the probable method of genesis of coal, many of the known types of polymeric structure could conceivably be present. Its relatively great resistance to hydrolytic agents appears, however, to render improbable some of these, such as ester, anhydride, acetal, or lactone. An ether-linked structure, such as has been suggested for lignin, a Bakelite type, or an addition polymer formed from unsaturated units seems more likely.

The determination of the exact character of the building units in bituminous coal and the nature of the forces which hold these units together present problems which as yet have been scarcely touched and offer a fertile field for chemical and physical investigation.

SUMMARY

Evidence is presented for the point of view that bituminous coal is a polymer. Cryoscopic measurements in catechol on the degradation products of a typical coal from the Pittsburgh seam indicate that the unit is of moderate molecular weight, 250 to 350. Significant yields of this fundamental building unit are obtained by thermal decomposition in the molecular still, by the action of solvents such as benzene, tetralin, or phenol at elevated temperatures, by hydrogenation, and by mild oxidation. The chief difference between the primary degradation products obtained by mild oxidation, the regenerated humic acids, and those recovered by thermal decomposition or hydrogenation, the bitumens, appears to lie in the presence in the humic acids of carboxyl groups, which confer alkali solubility and hydrophilic properties. The probable chemical nature of these primary degradation products and the possible methods by which the units combine are discussed.

REFERENCES

- (1) ASBURY: Ind. Eng. Chem. **26**, 1301 (1934).
- (2) ASBURY: Ind. Eng. Chem. **28**, 687 (1936).
- (3) BIGGS: J. Am. Chem. Soc. **58**, 1020 (1936).
- (4) BIGGS: J. Am. Chem. Soc. **58**, 487 (1936).
- (5) BONE, HORTON, AND WARD: Proc. Roy. Soc. London **127A**, 508 (1930).
- (6) BONE, PARSONS, SAPIRO, AND GROOCKOCK: Proc. Roy. Soc. London **148A**, 521 (1935).
- (7) CAROTHERS: Chem. Rev. **8**, 354 (1931).
- (8) CAROTHERS: Chem. Rev. **8**, 388, 405 (1931).
- (9) FISCHER, F., PETERS, AND CREMER: Brennstoff-Chem. **14**, 181 (1933).
- (10) FISCHER, F., AND SCHRADER: Ges. Abhandl. Kenntnis Kohle **5**, 470 (1920).
- (11) FREUDENBERG: Ber. **63**, 2713 (1930).
- (12) FUCHS: Die Chemie der Kohle, p. 445. Springer, Berlin (1931).
- (13) JUETTNER AND HOWARD: Ind. Eng. Chem. **26**, 1115 (1934).
- (14) JUETTNER AND HOWARD: Ind. Eng. Chem. **26**, 1117 (1934).
ASBURY: Ind. Eng. Chem. **26**, 1306 (1934).
- (15) LOWRY: Ind. Eng. Chem. **26**, 321 (1934).
- (16) PETERS AND CREMER: Z. angew. Chem. **47**, 576 (1934).
- (17) POTT, BROCHE, AND SCHEER: Fuel **13**, 91 (1934).
ASBURY: Ind. Eng. Chem. **28**, 687 (1936).
- (18) SCHRAUTH: Brennstoff-Chem. **4**, 161 (1923).
- (19) SIDGEWICK AND EUBANK: J. Chem. Soc. **117**, 396 (1920).
- (20) SMITH AND HOWARD: J. Am. Chem. Soc. **57**, 512 (1935).
- (21) JUETTNER, SMITH, AND HOWARD: J. Am. Chem. Soc. **57**, 2322 (1935).

MOLECULAR PROPERTIES OF LIGNIN SOLUTIONS¹

FROM VISCOSITY, OSMOTIC PRESSURE, BOILING-POINT RAISING, DIFFUSION,
AND SPREADING MEASUREMENTS

D. L. LOUGHBOROUGH AND ALFRED J. STAMM

*Forest Products Laboratory,² Forest Service, U. S. Department of Agriculture,
Madison, Wisconsin*

Received June 11, 1936

Recent chemical researches (2, 12) indicate that lignin, as isolated from previously extracted wood by several different methods, is a reproducible material with rather definite properties. It has ten polar groups, methoxyl and hydroxyl, for each empirical molecular weight unit of approximately 900, the proportion of each varying somewhat with the source of the lignin and the means of its isolation (12). The presence of unsaturated groups has also been demonstrated. An uncertainty still exists as to whether the basic part of the molecule is made up of aromatic or furan units.

The work reported here was undertaken with the hope that physical data on lignin solutions would aid in the further characterization of lignin. Previous measurements of the molecular weight of lignin are meager and have been made chiefly on lignin derivatives which, because of the nature of the preparations and the drastic solvents used, must have been degraded. These values range from 200 to 2000 (1, 6, 7, 9, 11, 17, 26, 27, 28, 29, 36). The most reliable value seems to be that of Samec (30) who, using a static osmotic pressure method, reported a value of 4000 for the molecular weight of Willstätter lignin dissolved in ammonium hydroxide. Spreading measurements have also been made to determine the thickness of lignin films on a water surface. Wedekind and Katz (37) obtained 10 A. U. for phenol lignin and Freudenberg (5) reports 20 A. U. for the sodium salt of the diazobenzenesulfonic acid derivative of cuprammonium lignin.

¹ Presented before the Thirteenth Colloid Symposium, held at St. Louis, Missouri, June 11-13, 1936.

Abstracted from a thesis submitted by D. L. Loughborough to the Faculty of the University of Wisconsin in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1936.

² Maintained at Madison, Wisconsin, in coöperation with the University of Wisconsin.

PREPARATION OF MATERIAL

The lignin used in this investigation³ was prepared from maple and spruce wood. The sawdust was extracted with alcohol-benzene mixture for two or three days to remove resins and fatty substances. This was followed in consecutive order by a thorough extraction in hot water, cold water, and ether. The lignin was isolated from the extracted sawdust in three different ways: (a) by the modified sulfuric acid method of the Forest Products Laboratory (31); (b) by extracting the lignin directly with methyl alcohol acidified with hydrochloric acid (6); and (c) by extracting in a sodium hydroxide-ethyl alcohol mixture (25). The soluble portions of the isolated lignin preparations were purified by alternate solution in alcohol and precipitation in water three or four times. In some cases the product was also precipitated in ether. The measurements reported here were made on the product after different numbers of precipitations, and in some cases the final product was electrodialed for forty-eight hours at 230 volts. The material was dried in a vacuum oven at 50°C. for more than forty-eight hours and stored over phosphorus pentoxide until needed. The solvents were of reagent quality, dried by standard drying methods.

The completely nitrated and methylated lignins were prepared from methyl alcohol-hydrochloric acid lignin. The nitrated lignin was prepared according to the method of Gilman (10) for nitrating furfural; the methylated lignin was prepared by the ordinary methylation process with dimethyl sulfate.

SOLUBILITY OF LIGNIN

The solubility of lignin in organic solvents depends to a large extent on the method used for isolating the lignin. When isolated by the sulfuric acid method, only about 12 per cent of maple lignin and less than 2 per cent of spruce lignin is soluble in methyl alcohol. Since the sulfuric acid method removes the lignin quantitatively, these fractions represent the fraction of the total lignin that may be brought into solution by this method. Both the alkali and methyl alcohol-hydrochloric acid methods yield from one-third to one-half of the total lignin content of the wood. Virtually all the yield is soluble in methyl alcohol after precipitation and washing free of alkali and acid. No chemical difference, however, has been found between the soluble and insoluble fractions of the isolated lignins. Thus the solubility differences are probably due to polymerization.

Since all the physical measurements considered in this study were made

³ Acknowledgment is made to E. E. Harris of the Forest Products Laboratory for the preparation of a number of the lignin samples and lignin derivatives used in this investigation. To him also are due thanks for many suggestions and advice on the chemical aspects of this problem.

on solutions of lignin, no definite conclusion can be drawn regarding the total isolated lignin, or the lignin as it occurs in the tree.

Lignin is somewhat soluble in many solvents, among which are the aliphatic alcohols and acids, methyl and ethyl acetate, acetone, and chloroform. Lignin that is air-dried after precipitation in water is insoluble in water, ether, benzene, or carbon tetrachloride. Although the solubility is not very great in most of these solvents, the amount that can be put into solution can be greatly increased by evaporation of the solutions. It is almost impossible to dissolve all the dry material added to the solvent, since some of the lignin almost invariably forms a tarry insoluble mass.

The solubility in chloroform is greatly increased by removing every trace of water. In the alcohols, on the other hand, the solubility is increased considerably by the addition of small amounts of water. For example, the direct solubility of alkali lignin in methyl alcohol was found to increase to a water content of approximately 18 per cent by volume and then to decrease with a further increase in water content.

All the solutions of dry lignin were clear. They showed no Tyndall cone unless treated in a way that causes precipitation, as when appreciable amounts of water are added. Solutions have been kept as long as two years without showing any cloudiness. Lignin dissolved in the foregoing solvents can thus be considered as forming true solutions.

VISCOSITY

A Bingham viscometer, flow time 1,164 sec. for water under 6 cm. of mercury, was rigidly mounted in a thermostated water bath held at $25^{\circ} \pm 0.02^{\circ}\text{C}$. The applied pressure was controlled from an auxiliary tank of 70 liters capacity. This tank could be filled to the desired pressure, closed from the air line, and held at this pressure for long periods of time. The pressure was read with a cathetometer to a tenth of a millimeter of mercury. Several measurements of the efflux time for flow in both directions were made at each pressure.

Poiseuille's law, in which the reciprocal of the efflux time is proportional to the pressure, was obeyed over the complete pressure range used. Over the concentration range used (0.2 to 8.0 per cent) there was no great deviation from the modified Einstein law

$$\frac{100 \eta_{sp}}{CV} = 2.5 \theta \quad (1)$$

where η_{sp} is the specific viscosity (increase in relative viscosity of the solution over that of the solvent), C is the concentration in grams per 100 cc. of solution, V is the specific volume of the solute, and θ is a constant, which

is unity for the ordinary Einstein equation. The expression $\frac{100 \eta_{sp}}{CV}$ has been designated by Kraemer (15) as the specific hydrodynamic volume. V was determined pycnometrically at 25°C. for sulfuric acid lignin and methyl alcohol-hydrochloric acid lignin dissolved in methyl alcohol and acetic acid. The values were in fairly good agreement, and average 0.75. The change in the specific viscosity per unit concentration with concentration for methyl alcohol-hydrochloric acid lignin in different solvents is given in figure 1. The curves are practically horizontal over an appreciable concentration range, with the expected upward curvature at higher concentrations in the case where higher concentrations were obtainable. It is uncertain if the curvatures in either direction at extremely low concentrations have any significance, though the deviations seem to be greater than the experimental error. The linear portions of the curves have been

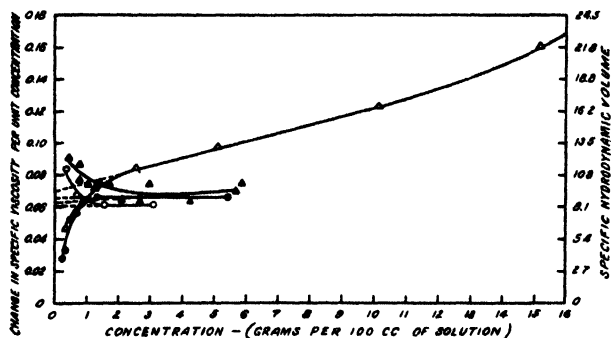


FIG. 1. Change in the specific viscosity per unit concentration with concentration for methyl alcohol-hydrochloric acid lignin. Δ , chloroform; \blacktriangle , acetone; \bullet , methyl alcohol; \circ , ethyl alcohol.

extrapolated to zero concentration in order to calculate the limiting values of θ , without regard to the curvature at low concentrations, as has been done by other investigators (16, 34). These values, as shown in table 1, are practically constant for all the solvents. Values of θ for sulfuric acid and alkali lignins are also given. These measurements were not made over a sufficient concentration range to make extrapolation advisable, so that they represent the directly calculated values. They are not in so good agreement as the values for methyl alcohol-hydrochloric acid lignin, but they do represent the order of magnitude of θ .

Three explanations are possible for the deviation of the data from the simple Einstein equation in which θ is unity. The first is that the departure may be due to solvation of the solute particle. The method of measuring the specific volume used does not give a true measure of the volume of the solvated particle. The constancy of θ , however, for quite

different solvents makes this factor, in all probability, of minor importance. The second explanation is that the equation is derived on the basis of no interaction between particles, a condition which would occur only at infinite dilution. Unfortunately, the extrapolation to zero concentration can not be definitely made until more accurate measurements at extremely low concentrations are available. The third explanation is that if the particles were not spherical, they would not be expected to obey the original Einstein equation derived on that basis. The equation has been extended to include differently shaped particles by Eisenschitz (4), Jeffery (13), and Kuhn (17, 18). The Eisenschitz equation for appreciably elongated elliptical particles when substituted in the modified

TABLE 1

Multiples of Einstein constant obtained for various lignin preparations from viscosity data at 25°C.

SOLVENT	VALUES OF $\frac{1}{2.5} \cdot \frac{100\eta_{sp}}{CV}$		
	Methyl alcohol-hydrochloric acid lignin*	Sulfuric acid lignin†	Alkali lignin†
Methyl alcohol	3 36	3 00	4 90
Ethyl alcohol		4 12	
Ethyl alcohol (few per cent water)	3 26		
n-Butyl alcohol		4 50	
n-Propyl alcohol		4 20	
Acetone	3 30	2 08	
Methyl acetate		2 60	
Chloroform	3 46		

* By extrapolation to zero concentration.

† From single measurements below 1 per cent concentration, by assuming η_{sp}/C as constant.

Einstein equation gives the shape factor l/a of the elliptical particles in terms of the multiple of the Einstein constant θ , thus

$$0.159 \frac{l}{a} \frac{1}{\log 2 \frac{l}{a}} = 2.5 \theta \quad (2)$$

This gives a shape factor for lignin of approximately 7.5. Although this shape factor is in a range for which there is no apparent reason for the validity of the equation, Theis and Bull (34) have found the relationship to be obeyed by stearic acid which, from x-ray and spreading measurements, has been shown to have a shape factor of this order.

If the specific viscosity is a function of the shape of the molecule, it

should vary with the temperature. At the higher temperatures the frequency of rotation about even the longest axes will be large in terms of the collision frequency, and a molecule will offer nearly spherical collision volume. The values of the specific viscosity should tend more and more toward that predicted by the Einstein equation. The plot of θ as a function of temperature over a small range is shown in figure 2. The extension of this curve could readily give a value of unity for θ at high temperatures.

Direct application of the Staudinger method (33) of determining the molecular weight from viscosity to these data is impossible, since no information is available on the lower molecular-weight homologues of lignin, if there are any. An idea of the magnitude of the molecular weight

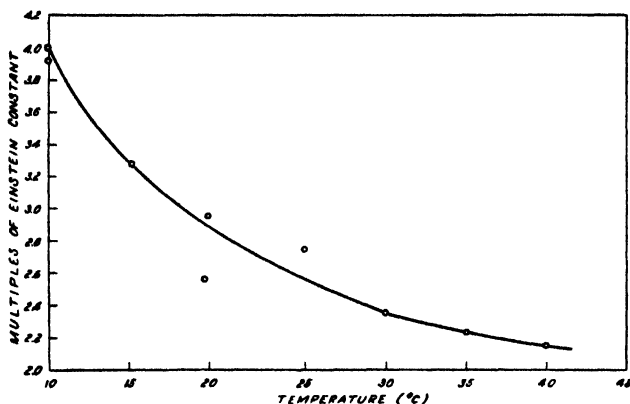


FIG. 2. Variation of the specific hydrodynamic volume of a sulfuric acid lignin in methyl alcohol with temperature.

m may be obtained by choosing a representative value for the constant in the equation

$$\frac{\eta_{sp}}{C} = Km \quad (3)$$

in which C is the concentration in terms of the weight of the repeating basic group and K is a constant. Taking the basic chemical molecular weight of lignin (900) as the repeating group and a value of K equal to that for rubber, 3×10^{-4} (33), the molecular weight obtained is 18,000. If the value of K of 10×10^{-4} for cellulose (33) is used, the molecular weight is 6000. These values can be thought of merely as an interesting speculation.

The viscosity data on lignin show conclusively that lignin is not a linear polymer such as cellulose, which has a value of θ of 280 to 400 (21). The lignin molecule, however, deviates definitely from spherical, a probable

shape factor being about 7.5. The approximate constancy of θ for different solvents indicates that lignin is probably not differently associated in the different solvents. Differences in solvation in the different solvents also appear to be small.

OSMOTIC PRESSURE

The measurement of molecular weight by osmotic pressure provides a method that is less affected by impurities than any of the other thermodynamic methods, such as freezing-point lowering or boiling-point raising. The method used was a modification of the dynamic method of Sørensen

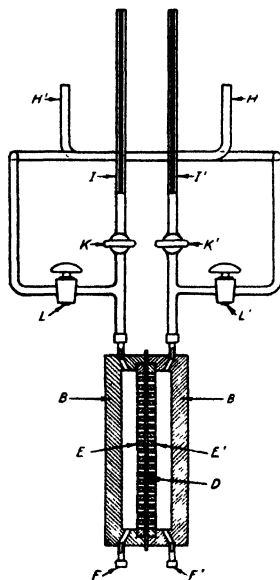


FIG. 3. The osmometer

(3, 32, 35), altered to give a better support to the membrane and to make possible the use of less material.

The osmometer (figure 3, side view) consists of two brass cells, B and B', 4 in. in diameter and 1 in. thick, with a hole 3 in. in diameter turned to a depth of $\frac{1}{2}$ in. in each. The cavities between the cells are separated from each other by two perforated brass disks, E and E', which rest on the circular flanges. The membrane D is held securely between these two disks. The rest of the apparatus serves in filling, applying the pressure, and measuring the flow. The osmometer is filled through F and F' (the primed letters indicate solution and the unprimed letters the solvent) by suction applied at H and H', the level of both solution and solvent being raised, free from bubbles, to the horizontal part of H. F and F' are

securely closed with brass screw caps. All stopcocks are closed and the system allowed to stand for eight or ten hours. This procedure allows any material of very small molecular weight to come to equilibrium before the measurements are made. The whole apparatus, with the stopcocks open, is then placed in a constant-temperature bath held at $25^{\circ} \pm 0.05^{\circ}\text{C}$. When thermal equilibrium has been established, stopcocks K' and L are closed, the pressure applied at H', and the flow measured in the capillary tube I by means of a cathetometer. If the applied pressure is greater than the osmotic pressure, the liquid will be forced across the membrane and up the capillary tube I. The rate of flow is proportional to the pressure in excess of the osmotic pressure, so that when the flow is zero, the applied pressure equals the osmotic pressure. Readings of the height of the men-

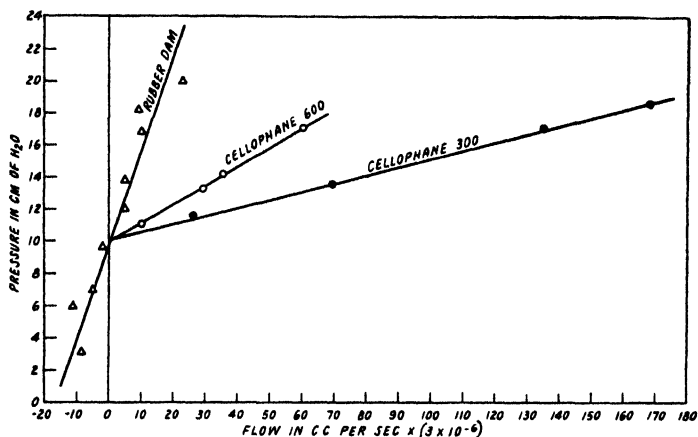


FIG. 4. Dynamic means of determining the osmotic pressure from the rate of flow under different hydrostatic pressures for methyl alcohol-hydrochloric acid lignin (0.00142 g. per cubic centimeter) in methyl alcohol.

iscus in I were measured every half-minute for 20 minutes, and these values were plotted against the time to determine the rate of flow. The rates of flow obtained under different applied pressures were plotted against the pressure and the curves extrapolated to zero flow, the intercept being the osmotic pressure.

Rubber dam and cellophane membranes were used. The cellophane membranes were of 600 and 300 gage. The cellophane was swollen in water, and the water replaced by the solvent. The fact that the osmotic pressure is independent of the membrane may be noted in figure 4, in which a typical plot of flow against pressure for a solution of methyl alcohol-hydrochloric acid lignin in methyl alcohol is given for all three membranes.

The molecular weights, as tabulated in table 2, were calculated from the

osmotic pressure on the basis of the van't Hoff law. The average molecular weight is, within experimental error, unchanged by the solvent, the method by which the lignin was isolated, the number of reprecipitations after the second in the purification, the fractionation, the temperature at which the measurement was made, the presence of small amounts of water or small amounts of salt, or the concentration.

The fact that elevation of the temperature does not affect the molecular weight indicates that the lignin molecule is not a loose aggregate of smaller molecules subject to thermal dissociation. No dissociation or polymerization occurs when small amounts of water are added. When sufficient salt is added to overcome any Donnan effect that might be present, the molecular weight is unchanged, indicating that there can not be any appreciable Donnan effect in the case of the electrolyte-free systems. Acetone and ethyl alcohol solutions of methyl alcohol-hydrochloric acid lignin were poured through a filter containing a small amount of activated charcoal. When this process was carried out rapidly, it was possible to halve the concentration. Molecular weights calculated from the osmotic pressure exerted by these solutions were definitely of the same order of magnitude as those calculated from the total fraction. Both the difficulty of performing the fractionation and the similar molecular weights measured indicate strongly that lignin forms monodisperse solutions. This is not in agreement with the results of Fuchs (8) for phenol lignins.

The most probable molecular weight from the measurements on maple lignin prepared by the three methods previously mentioned is 3900 ± 300 . This is very close to the value reported by Samer (30), and also approximately four times the empirical molecular weight (4×900). Completely methylated and nitrated lignins show increases in molecular weight that can be accounted for on the chemical basis. The fact that the different lignin preparations, which represent different portions of the total lignin, give similar molecular weights is a strong indication that the lignin is not a mixture of molecular species with appreciable variation in molecular weight, for it is highly improbable that each of the preparations should contain the same molecular distribution.

BOILING-POINT RAISING

A few measurements of the boiling-point raising of lignin in chloroform and acetone were made. In this work two sets of the modified⁴ Cottrell boiling-point raising apparatus were used so as to require only 10 cc. of solution. They were heated on an electric hot plate by inserting the end of each into a form-fitting brass thimble so that only the part beneath the inverted funnel was heated. The tubes were inserted through holes in an

⁴ This was done by H. D. Tyner of the Forest Products Laboratory.

TABLE 2
Molecular weight of various lignin preparations from osmotic pressure measurements at 25°C.

TYPE OF LIGNIN	SOLVENT	CONCENTRATION grams per cc.	MEMBRANE	REMARKS	MOLECULAR WEIGHT
Maple lignin (methyl alcohol-hydrochloric acid)	Methyl alcohol	0.001-0.01	Cellophane 600	In various states of purification	3800* \pm 300
	Methyl alcohol	0.01824	Cellophane 600	Electrodialyzed	4050
	Methyl alcohol	0.00125	Cellophane 600	At 39.6°C.	3500
	Methyl alcohol	0.00166	Cellophane 600	+10 per cent water	3940
	Methyl alcohol	0.00237	Cellophane 600	+10 per cent water	4200
	Methyl alcohol	0.00142	Rubber dam		3600
	Methyl alcohol	0.00142	Cellophane 600		3850
	Methyl alcohol	0.00142	Cellophane 300		3750
	Methyl alcohol	0.00075	Cellophane 300		3900
	Methyl alcohol	0.00125	Cellophane 300		3900
	Ethyl alcohol	0.00274	Cellophane 600		4900
	Ethyl alcohol	0.00120	Cellophane 600	Charcoal fractionated	4000
	Acetone	0.00268	Cellophane 600		3600
	Acetone	0.00235	Cellophane 600		3720
	Chloroform	0.00504	Cellophane 600	Charcoal fractionated	4050
Total average.					3870
Maple lignin (sulfuric acid)	Methyl alcohol	0.00913	Cellophane 600		4560
	Methyl alcohol	0.00754	Cellophane 600		3920
	Methyl alcohol	0.00913	Cellophane 300		4100
	Methyl alcohol	0.00408	Cellophane 300	0.045 N with NaCl	3930
	Ethyl alcohol	0.0960	Cellophane 300		3420
Total average.					3985

Maple lignin (alkali)	Methyl alcohol	0 00717	Cellophane 600	4500
	Ethyl alcohol	0 00105	Rubber dam	3680
	Total average			4090
Fully methylated maple lignin (alcohol-hydrochloric acid)	Methyl alcohol	0 00245	Cellophane 600	4500
	Acetone	0 00459	Cellophane 600	4300
	Acetone	0 00240	Cellophane 600	4200
	Total average.		4300
Fully nitrated maple lignin (alcohol-hydrochloric acid)	Ethyl alcohol	0 00450	Cellophane 600	3940
Spruce lignin (alcohol-hydrochloric acid).	Methyl alcohol	0 00242	Cellophane 600	3520
	Methyl alcohol	0 00242	Cellophane 600	3500
	Total average .		..	3510

* Average of ten determinations.

asbestos board up to the liquid level to eliminate the heating of the upper part of the apparatus by other than the boiling liquid and vapor. Measurements of the temperature were made with Beckmann thermometers when solvent was in both tubes and when solvent was in one and solution in the other. Thermometer readings were taken after different lengths of time, and the values obtained after experimental constancy was attained were averaged. The molecular weights calculated from the boiling-point raising, together with the probable error due to fluctuations of the temperature, are given in table 3. Considerable difficulty was encountered

TABLE 3

Molecular weight of various lignin preparations from boiling-point raising measurements

TYPE OF LIGNIN	SOLVENT	CONCENTRATION	MOLECULAR WEIGHT	ERROR
		<i>grams per gram of solvent</i>		
Maple lignin (methyl alcohol-hydrochloric acid).....	Chloroform	0.0672	3780	±100
	Chloroform	0.0336	3620	±400
	Chloroform	0.0308	3760	±200
	Chloroform	0.0154	3670	±500
	Acetone	0.0952	3180	±300
	Acetone	0.0472	3460	±500
Maple lignin (sulfuric acid).....	Chloroform	0.00605	3160	±1000
Maple lignin (alkali).....	Chloroform	0.0432	3510	±400
	Chloroform	0.0216	3810	±300
	Chloroform	0.0093	3410	±500
Fully methylated maple lignin (methyl alcohol-hydrochloric acid).....	Chloroform	0.0101	4220	±700
Spruce lignin (methyl alcohol-hydrochloric acid).....	Chloroform	0.00598	3640	±1000

in making the measurements upon spruce lignin, because it separated from solution in higher concentrations. Even in the comparatively low concentration reported the solution showed a slight Tyndall cone. Similar difficulty in obtaining consistent results was encountered with the sulfuric acid lignin. Only the value most consistent with the other data is given. All the measurements on methyl alcohol-hydrochloric acid lignin are given, however. In general, the agreement with the osmotic-pressure values is good, although the experimental error seems to be somewhat greater. The data give a further indication that temperature does not affect the

molecular weight and that it is inappreciably affected by the concentration.

DIFFUSION

The measurement of the diffusion constant was carried out by the method of Lamm (19, 20), in which the rate of change of concentration is measured by following the rate of change of index of refraction. The latter is determined by measuring the displacement of the lines of a uniform, transparent scale placed behind the diffusion cell, the displacement being caused by the index of refraction gradient in the cell. Photographs of the scale, using the monochromatic light from a sodium vapor lamp for illumination, were taken every half-hour for a period of about four hours with a long focus camera to avoid distortion of the image.

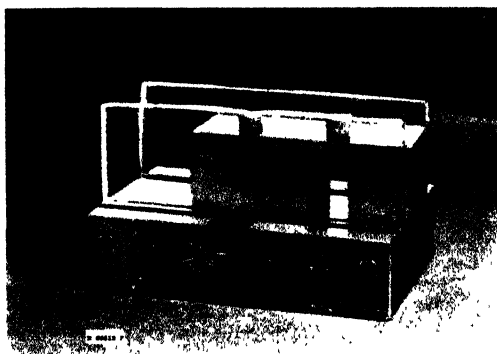


Fig. 5. The diffusion apparatus

The diffusion apparatus was constructed of two blocks of monel metal. The larger of two blocks had two grooves $3/4$ in. deep and $3/8$ in. wide running the length of the block, $1/4$ in. from the edge. Plate glass windows were securely fastened in these grooves by means of a brass spring arrangement, the pressure of which was adjusted by set screws (figure 5). Slots $1/2$ in. wide and $1/2$ in. deep were cut across each of the blocks, serving as the cells when the faces are closed by the plate glass. The apparatus was put together in the position shown in the figure, the upper cell being filled with solvent and the lower with solution by means of openings in the top of the smaller block, after which they were closed with corks as shown in the illustration. In the case of the chloroform solutions the procedure was reversed, since the solvent is more dense than the solute. The apparatus was fastened securely to the bottom of a brass air bath that had plate glass windows at each end. The air bath was surrounded completely by a water bath held at $25^\circ \pm 0.02^\circ\text{C}$. The apparatus was allowed to reach

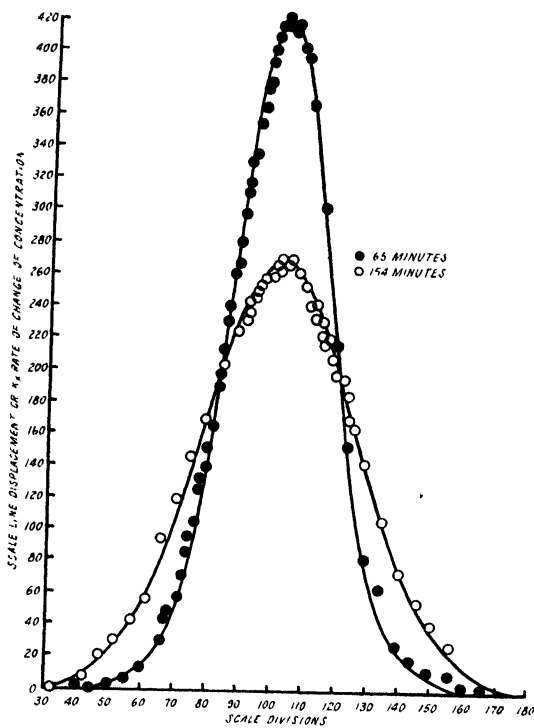


FIG. 6. Diffusion curves for sugar solutions. Scale displacement as a function of the height in the diffusion cell.

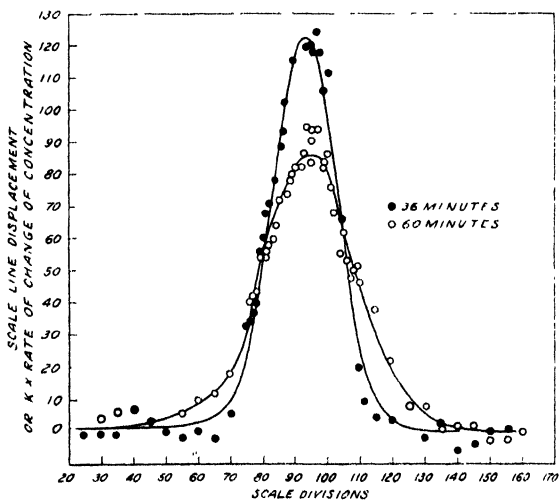


FIG. 7. Diffusion curve for methyl alcohol-hydrochloric acid lignin in methyl alcohol. Scale displacement as a function of the height in the diffusion cell.

thermal equilibrium, for which two hours usually was considered sufficient, the air being stirred constantly. Then the upper cell was pushed over the lower by a steadily moving screw. The boundary formed between them was very sharp, as may be noted by the fact that the diffusion constant measured was independent of the time, even for times as short as half an hour.

The displacement of each line on the photographs was measured with a comparator to 0.002 cm., and the displacement plotted against the height

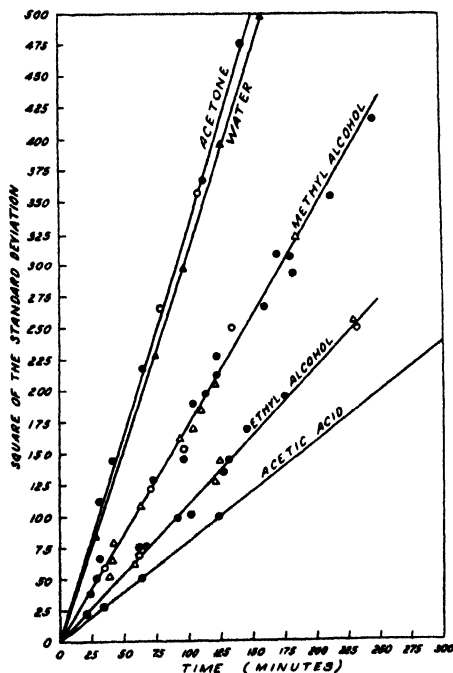


FIG. 8. Diffusion data in terms of the relationship between the square of the standard deviation and the time for sugar in water solutions and various lignin preparations in several organic solvents. ○, sulfuric acid lignin (0.2–0.4 per cent); ●, methyl alcohol–hydrochloric acid lignin (0.1–0.6 per cent); △, alkali lignin (0.3 per cent); ▲, sugar (0.5 per cent).

in the cell. Representative plots for sugar and for lignin are shown in figures 6 and 7. On the basis of the index of refraction being proportional to the concentration, these graphs are, except for a scale factor, a plot of the rate of change of concentration against the height in the cell. The solution of Fick's law for diffusion taking place under these conditions is a normal probability curve, the standard deviation σ of which is related to the diffusion constant D through the following equation:

$$\frac{K\sigma^2}{2t} \quad (4)$$

where t is the time. The standard deviation was determined by finding the normal curve of known standard deviation that most closely matched the experimental points. The lines in figures 6 and 7 represent the normal curves chosen to represent those data. The squares of the standard deviation were plotted against the time, and the diffusion constant was determined from the slope. When the concentrations were of the order of one-half of 1 per cent or more, the displacement of the lines was so great as to make accurate determinations impossible. Only those curves were used to determine the standard deviation for which most of the scale lines could be read with certainty. A plot for sugar and the various lignin preparations in several of the solvents is shown in figure 8. The diffusion constant obtained for sugar is 4.58×10^{-6} sq. cm. per second, which is in good agreement with the accepted values found in the literature.

The determination of the molecular weight of lignin was made from the diffusion constant by means of Einstein's diffusion equation

$$D = \frac{RT}{N} \cdot \frac{1}{6\pi\eta r} \quad (5)$$

The molecular weights so determined are shown in table 4. A single run with a McBain-Northrup diffusion cell (22, 23) was made on a solution of methyl alcohol-hydrochloric acid lignin in methyl alcohol at a concentration of 0.00248 g. per cubic centimeter. The cell constant was determined with sugar. A molecular weight of 9500 was obtained. The molecular weights for all the lignins in all the solvents are nearly identical, but they are considerably higher than the molecular weights determined by osmotic-pressure data. There are two reasons that might account for this difference. First, the lignin solution might be a mixture of different molecular species. The osmotic pressure gives a molecular weight that depends upon the number of particles in the solution, whereas the diffusion constant gives a molecular weight that depends upon a weight average of the particles. Any appreciable deviation from monodispersion would result in higher calculated molecular weights from diffusion than from osmotic pressure, because the larger particles would have the dominating effect in the former measurements and the smaller particles in the latter (21). Several reasons have already been given to indicate that the lignin solutions approach monodispersion. The diffusion data also give further evidence of monodispersion. If the solutions were polydisperse, each species would diffuse at its own rate and its data would fall on a normal curve whose shape would depend on the weight and the number of particles of that particular species. The measured curve would be a weighted sum of these separate curves. This sum would probably not be normal, though it might approach normal if there were a great many particles of nearly equal molecular weights. The fitting of the data to a normal curve

can not be done with enough accuracy to show small departures from normal, but the agreement, as shown in figures 6 and 7, is very good. Also the plot of the square of the standard deviation against the time is linear over long periods. If the system were polydisperse this would not be true. Thus appreciable deviations from monodispersity are highly improbable.

If the molecules were not spherical, the use of the Einstein equation would be unjustified. Though the departure from spherical, as indicated by viscosity data, is small for the lignin molecule, the difference between

TABLE 4

Molecular weight of various lignin preparations from diffusion measurements at 25°C.

TYPE OF LIGNIN	SOLVENT	MOLECULAR WEIGHT	ERROR
Maple lignin (methyl alcohol-hydrochloric acid)	Methyl alcohol	10,000	±200
	Ethyl alcohol	10,000	±200
	Acetic acid	9,500	±500
	Chloroform	10,500	±500
Maple lignin (sulfuric acid)	Methyl alcohol	11,000	±1000
	Methyl alcohol (0.045 <i>N</i> with NaCl)	11,000	±500
	Methyl alcohol (+11 per cent water)	10,000	±500
	Ethyl alcohol	12,000	±1000
	Acetone	12,000	±600
Maple lignin (alkali)	Methyl alcohol	10,000	±500
	Ethyl alcohol	9,000	±500
Spruce lignin (methyl alcohol-hydrochloric acid)	Methyl alcohol	7,350	±300
Fully methylated maple lignin (methyl alcohol-hydrochloric acid lignin)	Acetone	9,500	±500

the molecular weights obtained by osmotic pressure and by diffusion increases rapidly with increasing ellipticity. Perrin (24) has developed a theory for the rotary diffusion of elliptical particles. The result is expressed in terms of the ratio of the time of relaxation for an elliptical particle (τ_1) and for a sphere (τ_0). The ratio of τ_1/τ_0 for a prolate spheroid rotating about its minor axis is

$$\frac{\tau_1}{\tau_0} = \frac{2}{3} \frac{1 - \rho^4}{(2 - \rho^2) \frac{\rho^2}{\sqrt{1 - \rho^2}} \log \frac{1 + \sqrt{1 - \rho^2}}{\rho} - \rho^2} \quad (6)$$

where ρ is the ratio of minor to major axis. If a somewhat similar relationship holds for linear diffusion, it should be possible to determine a shape factor for the lignin molecule. If the true molecular weight of lignin is taken as 3900, the diffusion constant, considering the molecule to be spherical, can be calculated. This diffusion constant is three-quarters of the measured values and, according to Perrin's theory, gives a shape factor of approximately 8. This is in as good agreement with the shape factor found from viscosity data as could be expected.

It is thus quite definite that the deviations of the molecular weight obtained by diffusion from the values obtained from osmotic pressure are due to a deviation of the molecule from a spherical shape rather than to the system being polydisperse.

Measurements, to be published later, made on the dispersion of the dielectric constant of chloroform solutions of lignin gave molecular weight

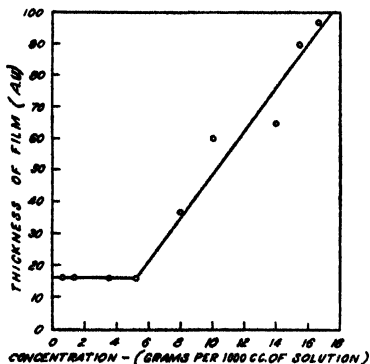


Fig. 9. Area covered per unit weight of methyl alcohol-hydrochloric acid lignin in chloroform as a function of the concentration.

values that were in good agreement with the values calculated from the diffusion constant. This was to be expected, since the dispersion of the dielectric constant is a measure of the rotary diffusion constant.

SPREADING MEASUREMENTS

Some concept of the dimensions of large organic molecules can be obtained from the measurement of the area covered by a material when spread on a liquid in which it is insoluble. If the molecular weight and density are known, the area per molecule as well as the thickness of the film can be determined.

Lignin was dissolved in chloroform and spread on water against the pressure of a thin film of lycopodium powder. When the area covered per gram of lignin was plotted as a function of the concentration, a limiting concentration of 0.005 g. per cubic centimeter was obtained, below which

the area covered per gram was a constant. This constant value corresponds to a film thickness of 16 A. U. (figure 9). If the molecular weight is taken as 3900, the area per molecule is 318 sq. A. U.

Spreading measurements were also made with a modified Langmuir film balance. The pressure exerted was practically zero until an area of 308 sq. A. U. per molecule, using several different concentrations, was reached. If the area was decreased slightly below this value the pressure rose very rapidly, the film collapsed, and the measurements were no longer reversible. Measurements upon 0.1 *N* hydrochloric acid solution gave similar results, and also measurements with nitrated lignin. If the two surface dimensions were equal, they would be equal to 17.6 A. U. and the molecule would be practically spherical. This is in disagreement with the previous findings reported here, which indicate a length from six to eight times the effective cross-sectional diameter. If the dimensions are taken as 16 A. U. by approximately 100 A. U. by 3 A. U., all the known data may be correlated.

SUMMARY AND CONCLUSIONS

Lignin isolated by three different methods and dissolved in a number of different organic solvents gives molecular weights of two magnitudes, one of which is 3900 ± 300 and the other $10,000 \pm 1,000$. The lower value was obtained by the osmotic-pressure and boiling-point raising methods, both of which give number average values and are independent of shape. The higher value was obtained by diffusion measurements, which give weight average values and are affected by shape. Two explanations for this difference are offered, one depending on the concept of polydispersity and the other depending on the departure of the molecules from a spherical shape. A number of reasons are given to show that the latter explanation is probably correct. The viscosity data indicate that the lignin dispersion approaches monodispersion, because of the practical constancy of the multiples of the Einstein constant at infinite dilution in the different solvents. The constancy of the molecular weight of all the lignin preparations in all the solvents, the nearness with which the actual diffusion data approach the theoretical standard deviation curves, and the non-variation of the diffusion constant with time are also given as evidence that the isolated lignin is a single molecular species. On the other hand, the magnitude of the multiple of the Einstein constant obtained from viscosity data and the deviation of the molecular weight calculated from the diffusion constant from the molecular weight from osmotic pressure both indicate that lignin has a shape factor of the order of 6 to 8. It thus appears that the true molecular weight is of the order of 3900 ± 300 , which is four times the empirical molecular weight. A possible set of molecular dimensions based on the film thickness obtained from spreading measurements and the shape factor is of the order of $3 \times 16 \times 100$ A. U.

The lignin preparations prepared by methods which deviate so appreciably and which give soluble fractions representing such different portions of the total lignin all approached monodispersion and gave identical molecular weights within experimental error. These phenomena certainly indicate that the soluble fractions of isolated lignin are similarly associated, namely, four times the empirical molecular weight of 900.

REFERENCES

- (1) BECHMANN, E., LIESCHE, O., AND LEHMANN, F.: *Z. angew. Chem.* **34**, Aufsatzteil, 285 (1921).
- (2) BRAUNS, O., AND HIBBERT, H.: *Pulp & Paper Mag. Can.* **34**, 187 (1933).
- (3) BÜCHNER, E. H., AND SAMWEL, P. J. P.: *Trans. Faraday Soc.* **29**, 32 (1933).
- (4) EISENSCHITZ, R.: *Z. physik. Chem.* **153A**, 78 (1931).
- (5) FREUDENBERG, K.: *Tannin, Cellulose, Lignin*, p. 131. Julius Springer, Berlin (1933).
- (6) FRIEDRICH, A., AND DIWALD, J.: *Monatsh.* **46**, 31 (1925).
- (7) FUCHS, W.: *Brennstoff-Chem.* **9**, 298, 363 (1928).
- (8) FUCHS, W.: *J. Am. Chem. Soc.* **58**, 673 (1936).
- (9) FUCHS, W., AND DAUR, R.: *Cellulosechem.* **12**, 103 (1931).
- (10) GILMAN, H.: *J. Am. Chem. Soc.* **56**, 464 (1934).
- (11) HÄGGLUND, E., AND URBAN, H.: *Cellulosechem.* **9**, 49 (1928).
- (12) HARRIS, E. E., SHERRARD, E. C., AND MITCHELL, R. L.: *J. Am. Chem. Soc.* **56**, 889 (1934).
- (13) JEFFERY, G. B.: *Proc. Roy. Soc. London* **102A**, 161 (1931).
- (14) KLASON, P.: *Ber.* **55B**, 448 (1922).
- (15) KRAEMER, E. O., AND SEARS, G.: *J. Rheol.* **1**, 231 (1930).
- (16) KRAEMER, E. O., AND VAN NATTA, F. J.: *J. Phys. Chem.* **36**, 3175 (1932).
- (17) KUHN, W.: *Z. physik. Chem.* **161A**, 1 (1932).
- (18) KUHN, W.: *Kolloid-Z.* **62**, 269 (1933).
- (19) LAMM, OLE: *Z. physik. Chem.* **138**, 313 (1928).
- (20) LAMM, OLE: *Z. physik. Chem.* **143**, 177 (1929).
- (21) LANSING, W. D., AND KRAEMER, E. O.: *J. Am. Chem. Soc.* **57**, 1369 (1935).
- (22) MCBAIN, J. W., AND LIU, T. H.: *J. Am. Chem. Soc.* **53**, 59 (1931).
- (23) NORTHRUP, J. H., AND ANSON, M. L.: *J. Gen. Physiol.* **12**, 543 (1929).
- (24) PERRIN, F.: *J. phys. radium* **5**, 497 (1934).
- (25) PHILLIPS, M.: *J. Am. Chem. Soc.* **49**, 2037 (1927).
- (26) PHILLIPS, M.: *J. Am. Chem. Soc.* **50**, 1986 (1928).
- (27) RASSOW, B., AND GABRIEL, H.: *Cellulosechem.* **12**, 227, 249, 290, 318 (1931).
- (28) RASSOW, B., AND WAGNER, K.: *Wochbl. Papierfabr.* **63**, 103, 161, 243, 303, 342 (1932).
- (29) ROUTALA, O., AND SEVON, J.: *Ann. Acad. Sci. Fennicae* **29A**, No. 11, 50 (1927).
- (30) SAMEC, M., AND PIKMAIER, B.: *Kolloid-Z.* **51**, 96 (1930).
- (31) SHERRARD, E. C., AND HARRIS, E. E.: *Ind. Eng. Chem.* **24**, 103 (1932).
- (32) SØRENSEN, S. P. L.: *Z. physik. Chem.* **106**, 1 (1919).
- (33) STAUDINGER, H.: *Trans. Faraday Soc.* **29**, 18 (1933).
- (34) THEIS, R. M., AND BULL, H. B.: *J. Phys. Chem.* **40**, 125 (1936).
- (35) VAN CAMPEN, P.: *Rec. trav. chim.* **50**, 915 (1931).
- (36) WAENTIG, P.: *Z. angew. Chem.* **41**, 493, 977, 1001 (1928).
- (37) WEDEKIND, E., AND KATZ, J. R.: *Ber.* **62B**, 1172 (1929).

THE COLLOIDAL NATURE OF ASPHALT AS SHOWN BY ITS FLOW PROPERTIES¹

R. N. TRAXLER AND C. E. COOMBS

The Barber Asphalt Company, Maurer, New Jersey

Received June 11, 1936

Although our knowledge of the physicochemical state of asphalt is quite incomplete, the notion of the colloidal nature of bituminous materials has been advanced by various authors. Richardson (21) did considerable pioneer work at a time when the modern conception of the colloidal state was just beginning to take form. Recently Nellensteyn (16, 17) and his coworkers have described asphalts as protected lyophobic sols in which the micelles, forming the dispersed phase, are composed of high molecular weight hydrocarbons of high carbon content, presumably enveloping nuclei of free carbon. It is generally assumed that the dispersed phase is composed of those substances, called asphaltenes, which are insoluble in 86° Baumé naphtha. The continuous or dispersing phase contains low molecular weight hydrocarbons which are soluble in 86° Baumé naphtha and are called petrolenes. Mack (14) considered asphalts as sols of asphaltenes in a mixture of asphaltic resins and oily constituents (petrolenes), and investigated the viscosity of various combinations of these phases. From his data he drew conclusions concerning the causes for the high viscosities shown by asphaltic materials.

Although there is some information in the literature regarding the viscosity of asphalt, there has been little work done in the direction of determining the presence and degree of the abnormal flow properties such as thixotropy, quasi-viscousness, and elastic effects which frequently prevail in, and are characteristic of, colloidal systems. On the basis of limited data some workers have asserted that asphaltic bitumen is truly viscous, while others have stated that it exhibits non-Newtonian flow characteristics. It is the purpose of the present paper to discuss the flow properties of asphalts of widely different source and type of processing, and to show how a knowledge of these properties substantiates the theory that asphalts are colloidal. The authors intend to show that the existence and magnitude of the anomalous flow characteristics depend not only on the type of bitumen, but also on the temperature at which the measurements are made,

¹ Presented at the Thirteenth Colloid Symposium, held at St. Louis, Missouri, June 11-13, 1936.

and on the method and degree of processing to which the asphalt has been subjected.

VISCOUS ASPHALTS

In our laboratory a number of asphalts have been studied in order to ascertain the effect of temperature and shearing stress on the experimentally determined viscosities. Measurements have been made from 15° to 130°C. by means of the modified Bingham-Murray plastometer (6, 19), the Bingham-Stephens alternating-stress method (7), the falling coaxial cylinder viscometer (20), and the conicylindrical rotation viscometer (15). All of these instruments as used in our laboratory have been described and discussed elsewhere (28). To complete the study of temperature effects, viscosities at temperatures as high as 190°C. have been measured by means of a Saybolt-Furol viscometer and the values in Furol seconds converted to poises (12).

TABLE 1
Identification of asphalts

DESIGNATION	SOURCE (TYPE)	PROCESS	PENETRATION AT 25°C., 100 g., 5 sec.	RING AND BALL SOFTEN- ING POINT °C.
A	Californian	Vacuum	55	47.2
B	Mexican	Vacuum	55	52.2
C	Mexican	Batch steam	62	52.2
D	Refined Trinidad native lake asphalt		4	96.7
E	Venezuelan	Batch steam	53	53.3
F	Venezuelan	Batch steam	41	61.9
G	Venezuelan	Air-blown	65	68.9
H	Venezuelan	Air-blown	94	57.2
I	Venezuelan	Air-blown	132	51.1

The viscosities of many steam- and vacuum-refined asphalts of paving consistency prepared from Californian, Venezuelan, Mid-Continent, and Mexican petroleums showed no dependence on the shearing stress employed over the large range of stresses studied at low (atmospheric) temperatures. However, with certain types of these asphalts deviations from viscous flow appear in the region of 40 penetration (3) at 25°C., 100 g., 5 sec., and are more exaggerated as the asphalt becomes harder. Vacuum-refined Californian asphalt exhibited Newtonian flow at atmospheric temperature even when it had been processed to as low as 35 penetration at 25°C., 100 g., 5 sec. (viscosity = 25×10^6 poises at 25°C.).

Table 1 serves to identify the various asphalts discussed in this paper with regard to source, method of processing, penetration, and Ring and Ball softening points.

In table 2 data on asphalts A and B, both of 55 penetration at 25°C., 100 g., 5 sec., are presented as typical examples of asphalts exhibiting truly viscous flow properties at both high and relatively low (atmospheric) temperatures.

The viscosities at the higher temperatures were measured in the Bingham-Murray apparatus, while the Bingham-Stephens alternating-stress method was used for the determination of the viscosities at low temperatures. The reproducibility of the above viscosity values is within ± 5 per cent. Within this limit the data in table 2 are typical of numerous asphalts whose viscosities are independent of the shearing stress employed.

TABLE 2
Data showing Newtonian flow for asphalts A and B

SHEARING STRESS		VISCOSITY	
Asphalt A at 100°C.		Asphalt B at 110°C.	
<i>dynes per cm.²</i>	<i>poises</i>	<i>dynes per cm.²</i>	<i>poises</i>
367.8	42.6	426.9	56.9
306.7	41.6	371.0	57.0
263.0	42.0	332.3	56.9
233.8	42.0	300.9	57.4
211.0	41.6	274.9	56.5
194.8	41.5	253.1	57.2
181.0	41.8	234.5	56.7
		218.4	57.2
Asphalt A at 20°C.		Asphalt B at 30°C.	
149,800	11.5×10^6	17,000	2.16×10^6
135,700	11.6×10^6	15,200	2.29×10^6
123,600	11.9×10^6	13,300	2.35×10^6
110,000	11.7×10^6	11,500	2.40×10^6
93,500	11.8×10^6	9,900	2.38×10^6
80,300	11.8×10^6	8,400	2.34×10^6

EFFECT OF TEMPERATURE ON VISCOUS ASPHALTS

It is generally assumed that asphalt is a system in which the solubility of the dispersed phase (asphaltenes) in the oily continuous phase (petrolenes) is influenced by temperature. At high temperatures the solubility is increased, except for free carbon if it is present. As the temperature is progressively lowered the two phases become more distinct and the colloidal properties of the system become more exaggerated. However, even at low temperatures the system usually is stable, the asphaltenes remaining dispersed owing to the protective action of the asphaltic resins. Various investigators are divided in their opinions as to whether this system has

the form of a suspensoid or of an emulsoid. The opinion has been expressed that the temperature-viscosity curves for asphaltic bitumen should have two marked points of transition, one where the system passes from the liquid to the semiliquid state, and the other where a transition occurs from the semiliquid to the solid state. From the rheological standpoint, this latter statement is ill-defined for, as far as flow properties are concerned, a transition from the true liquid state to anything approximating the solid state means a change from purely viscous properties to definitely plastic behavior, involving yield values and mobilities rather than viscosities. From the numerous data collected in our laboratory no asphalt has been found to possess plastic properties as defined above.

Nellensteyn and Roodenburg (18) have shown points of inflection in the relation between surface tension and temperature, while Klinkmann (13) and Spiers (26) have shown such transition points in their temperature-

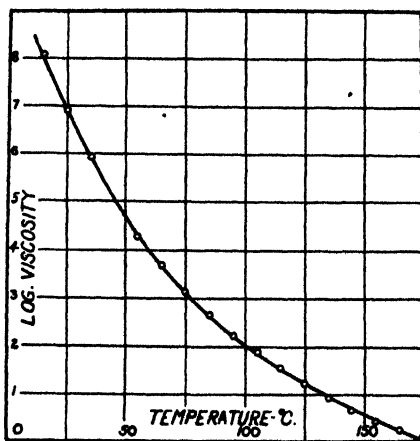


FIG. 1. Variation of viscosity of asphalt C with temperature

viscosity relationships for bitumen and tar. On the other hand, there is an abundance of data which shows that there is a distinct continuity throughout the viscosity-temperature curves. Evans and Pickard (9), Eymann (10), Pochettino (20), and Rodiger (22) have all given data supporting the latter statement. Saal (24) has recently shown that there is no break in the relation between temperature and surface tension for asphaltic bitumen.

In our laboratory the viscosities of fourteen asphalts of widely different origins, processed differently and to various degrees, have been measured from 15° to 190°C. Some of these data have been reported elsewhere (19, 25). The viscosities from 15° to 35°C. were measured by the alternating-stress method (7), from 40° to 130°C. by the modified Bingham-Murray apparatus (19), and above 130°C. with a Saybolt-Furol viscometer (2). The Furol seconds were converted to absolute c.g.s. units

(poises) (12). The type of data obtained is illustrated by figure 1, which shows the logarithm of the viscosity for asphalt C plotted against the temperature in degrees Centigrade. In none of the fourteen asphalts is there any indication of a sudden break in the viscosity-temperature relationship.

The fact that no sudden changes occur in the log viscosity versus temperature ($^{\circ}\text{C}.$) relation does not discount the notion that as the temperature is lowered, the asphaltenes gradually separate from true solution with the petrolenes to give rise to a stable system whose colloidal properties become more pronounced as the temperature decreases. The facts indicate that the transition from a condition approximating true solution to a distinctly colloidal state is so gradual that no sudden change in physical properties occurs. From a plot such as that shown in figure 1 it is evident that the so-called "softening point", which is of value to bituminous technologists, does not represent a temperature at which the viscosity changes sharply. It has already been pointed out (1) that the Ring and Ball softening point (4) is merely the temperature at which any asphalt attains a particular viscosity (approximately 12,000 poises). Saal (23) states that the Ring and Ball softening point may correspond to a viscosity value somewhere between 10,000 and 20,000 poises.

At atmospheric temperatures (15° to $40^{\circ}\text{C}.$), a range to which paving asphalts are subjected in use, a plot of the logarithm of viscosity against temperature in degrees Centigrade is a straight line within the limits of experimental error. Therefore, for this range, viscosity and temperature may be related by the expression

$$\log \eta = mt + b \quad (1)$$

where η = viscosity in poises, t = temperature ($^{\circ}\text{C}.$), and m and b are constants. For the higher temperatures where the viscosities vary from 1 to 5 poises, a consistency range in which asphalts are usually processed, the same type of equation applies.

An asphalt viscosity index, which evaluates the susceptibility of asphalts to temperature changes in terms of percentage decrease of viscosity (in poises) for a $1^{\circ}\text{C}.$ rise in temperature, has been derived (27), using the slope m of equation 1. This index is expressed as

$$\text{A.V.I.} = 100 (10^m - 1) \quad (2)$$

Experimentally, it is only necessary to measure the viscosities η_a and η_b at two temperatures t_a and t_b ($^{\circ}\text{C}.$) within the range where equation 1 is valid. Then,

$$\text{A.V.I.} = 100 \left[\left(\frac{\eta_a}{\eta_b} \right)^{1/(t_a - t_b)} - 1 \right]^* \quad (3)$$

* In actual practice the A.V.I. is most readily calculated from the expression $100 (\text{antilogarithm of the slope "m"} - 1)$.

Since the viscosity of asphalt diminishes with increasing temperature the values of the A.V.I. are negative, but from the definition given above the sign may be ignored. For asphalt C, shown in figure 1, the A.V.I. changes from 20.5 at the low service temperatures to 4.4 at the high processing temperatures. Thus, a great decrease in both viscosity and susceptibility to temperature change occurs with a large rise in temperature.

THIXOTROPY IN ASPHALTS

Numerous cases have been found where an initial working of the asphalt sample at a high stress was required before a constant viscosity value was

TABLE 3

Viscosity data showing presence of thixotropy in asphalt D at 50°C.

DIRECTION OF MOVEMENT*	SHEARING STRESS	VISCOSITY
	<i>dynes per cm.²</i>	<i>poises × 10⁻⁴</i>
In	145,000	23.6
Out	144,000	21.0
In	144,000	18.9
Out	144,000	18.2
In	144,000	17.4
Out	143,000	17.1
In	143,000	16.8
Out	143,000	16.0
In	143,000	16.0
Out	143,000	16.7
In	143,000	15.9
Out	124,000	16.4
In	124,000	15.6
Out	113,000	16.7
In	113,000	15.7
Out	92,800	16.5
In	92,800	15.9
Out	82,300	16.3
In	82,300	16.0

* The first "out" movement is never recorded because of difficulties in focusing, etc.

obtained. After a variable amount of structure, depending on the nature of the asphalt, was removed from the sample by the application of mechanical shear, the viscosity values for all stresses less than that initially used were constant. This phenomenon of thixotropy or breakdown of structure under the influence of mechanical working has been observed in many colloidal systems, especially when the concentration of the dispersed phase is appreciable. A typical case of thixotropy is found in the viscosity data for asphalt D given in table 3. The measurements on this asphalt were made using the alternating-stress method.

It will be noted that after the initial "working" period, the viscosity of this asphalt decreases to a value which remains essentially constant over a range of decreasing shearing stresses. The viscosity value corresponding to the "in" movement, for a given shearing stress, is always lower than that corresponding to the "out" movement. This behavior probably is caused by the elasticity of the material.

AGE-HARDENING OF ASPHALTS

An interesting and important manifestation of thixotropy is the phenomenon of age- or time-hardening of asphalts. Asphalt technologists know that if the penetration of a sample of asphalt is obtained immediately after cooling and again on the same undisturbed sample at intervals of several days, the asphalt will be found to have become harder with the passage of time. Remelting the sample causes the asphalt to return to its original consistency.

TABLE 4
Increase in viscosity of asphalt E with time

TIME	VISCOSITY	TIME	VISCOSITY
<i>hours</i>	<i>poises $\times 10^{-4}$</i>	<i>hours</i>	<i>poises $\times 10^{-4}$</i>
4	7.54	317	9.38
25	7.80	820	11.0
52	8.21	2232	12.1
77	8.56	4455	12.7
148	8.89	9100	14.2
		5*	8.3

* Remelted sample.

Measurement of viscosity in absolute units offered a sensitive method of evaluating this age-hardening phenomenon (29). The falling coaxial cylinder viscometer (20, 28) was particularly well adapted to such an investigation, because several instruments could be filled simultaneously with the same asphalt and stored at a constant temperature, and determinations of the viscosity could be made at any desired intervals of time. Ten or twelve instruments were usually filled with a particular asphalt. The viscometers and contents were stored in a cabinet maintained at $25^{\circ} \pm 0.5^{\circ}\text{C}$. At increasing intervals of time samples were removed from the cabinet and the viscosities measured at 25°C ., using a rather low shearing stress (7200 dynes per cm^2). After each measurement was completed the sample was discarded. Table 4 gives the data obtained using asphalt E.

The first value obtained (at the end of four hours) is unaccountably high, but the remaining nine values fall very close to a straight line when log viscosity is plotted against log time. The sample which had aged for 9100 hours was remelted in the viscometer, cooled, and the viscosity de-

terminated at the end of five hours, with the result shown at the bottom of table 4. It is evident that after aging for over one year a large percentage of the structure which had developed could be destroyed by heat.

The phenomenon of age-hardening is apparently thixotropic in its nature, because by the application of a high shearing stress in a rotating-cylinder viscometer the viscosity of an aged asphalt can be reduced just as is done by heating.

TABLE 5
"Equilibrium viscosities" of quasi-viscous asphalt F at 25°C.

APPROXIMATE TIME OF WORKING	MEAN SHEARING STRESS	RATE OF SHEAR	"EQUILIBRIUM VISCOSITY"
minutes	dynes per cm. ²	reciprocal seconds $\times 10^4$	poises $\times 10^{-3}$
35	11,600	5.72	20.3
30	34,800	17.6	19.9
60	69,600	40.6	17.3
100	138,700	114.	12.2

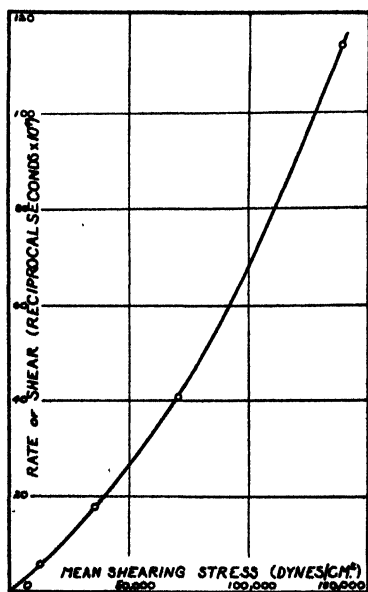


Fig. 2. Non-Newtonian flow of asphalt F at 25°C.

NON-NEWTONIAN FLOW

When a system possesses sufficient internal structure to cause the appearance of marked thixotropic effects, other anomalous flow characteristics often become apparent. At a particular shearing stress such a system must be worked in a given direction until a constant rate of movement is obtained. From this an "equilibrium viscosity" may be calculated.

However, the "equilibrium viscosity" decreases with increasing shearing stress, and a plot of the rate of shear versus shearing stress yields a curvilinear relationship passing through the origin. This phenomenon has been called non-Newtonian flow, and the materials are said to be quasi-viscous.

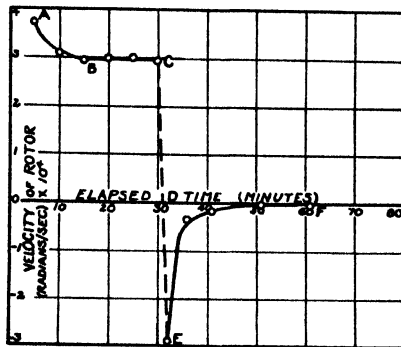


FIG. 3. Elastic effects in asphalt F at 25°C. Mean shearing stress = 34,800 dynes per square centimeter.

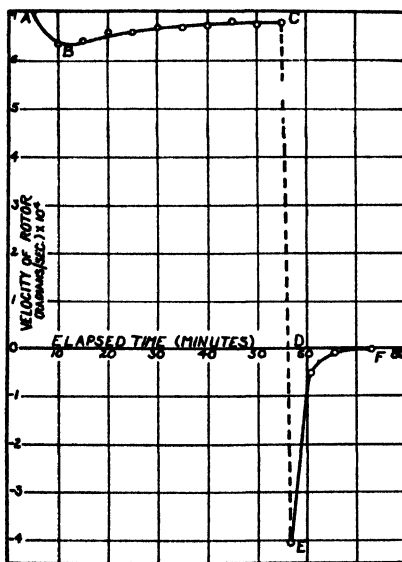


FIG. 4. Elastic and thixotropic effects in asphalt F at 25°C. Mean shearing stress = 69,600 dynes per square centimeter.

This type of flow indicates that the system possesses some rigidity, but the material cannot be called a plastic solid in the sense in which Bingham (5) uses the term. A "yield value" would have little physical significance since it would depend completely on the shearing stress at which it would

be determined. Further, the "yield value" would be zero when the rate of shear is zero.

Table 5 and figure 2 show data for asphalt F, a steam-refined asphalt of paving consistency, which exhibits a marked quasi-viscous nature. The measurements were made in the conicylindrical rotation viscometer (15, 28) at 25°C. Only the final "equilibrium viscosities" are recorded.

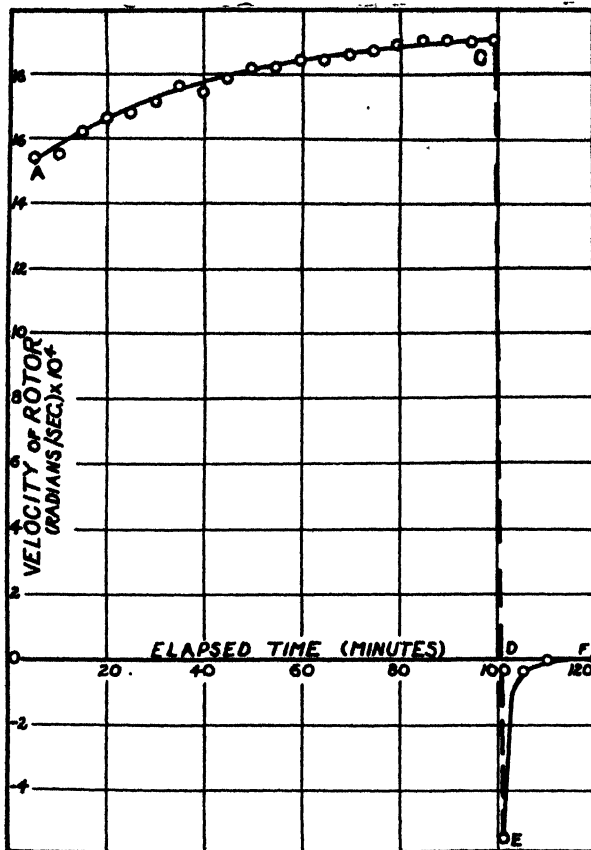


FIG. 5. Elastic and thixotropic effects in asphalt F at 25°C. Mean shearing stress = 138,700 dynes per square centimeter.

ELASTIC EFFECTS

Figures 3, 4, and 5 give some additional information concerning the flow properties of asphalt F. The rate of movement of the inner cylinder (radians per second $\times 10^{-4}$) is plotted against time in minutes for the last three shearing stresses given in table 5. If the material were purely viscous, the rate of movement would be independent of the period of working. However, it is observed (figure 3) that at the low stress (34,800 dynes per cm.²) the rate of movement of the inner cylinder is initially high and with

time decreases asymptotically to a constant value. The same behavior was noted for a shearing stress of 11,600 dynes per cm.² Such a phenomenon has been recognized in other materials as an elastic fore-effect by Braunbek (8) and by Ferry and Parks (11), et al. The initial elastic displacement is gradually obscured by the viscous deformation, and the rate of movement eventually becomes constant. The "equilibrium viscosity" given in table 5 is calculated from this constant rate. At point *C* in figure 3 the stress is suddenly removed from the sample and an elastic return is effected, the inner cylinder of the viscometer rotating in the reverse direction of its own accord. The rate of reverse movement is shown by curves *DE* and *EF*.

At a higher stress (69,600 dynes per cm.²) the same elastic fore- and after-effects are noted (figure 4). However, this stress is high enough so that the initial elastic fore-effect is partially masked by the breaking-down of structure within the sample. As the internal structure is destroyed by the mechanical shearing the rate of movement of the inner cylinder increases and finally becomes essentially constant. This constant rate is again used to calculate the "equilibrium viscosity" recorded in table 5.

When the high stress (138,700 dynes per cm.²) is used (figure 5), the initial elastic effect is entirely obscured by the viscous deformation and break-down of structure within the asphalt. However, it is evident that the system still possesses some structure, even after being subjected to a high stress for 100 minutes, because an elastic return is noted when the shearing stress is removed from the sample.

DEPENDENCE OF ANOMALOUS FLOW PROPERTIES ON THE DEGREE OF PROCESSING

It is known that as the processing of an asphalt continues the material becomes harder, resulting in a lower penetration and an increased percentage of asphaltenes (dispersed phase). In conjunction with this fact we have found that in air-blown asphalts of the type represented by asphalts G (65 penetration), H (94 penetration), and I (132 penetration), the harder the asphalt, the greater the deviation from Newtonian flow. Comparisons of these asphalts were made at approximately equal ranges of *rate of shear*, for it seems reasonable that the magnitude of thixotropic and quasi-viscous effects should depend on the rate at which the samples are sheared. If, on the other hand, we had compared these asphalts of widely different "viscosities" at a given range of shearing stresses, the low viscosity asphalt (132 penetration) would have been subjected to much higher rates of shear than the asphalt of highest viscosity (65 penetration). Thixotropic and quasi-viscous effects in the higher viscosity asphalts, as evidenced from a comparison of the final "equilibrium viscosities" of these three different asphalts, would therefore have been underestimated.

For a complete study of elastic effects, however, all samples should be run at exactly the same shearing stresses. Since we are interested primarily in the thixotropic and quasi-viscous characteristics of these materials in the present work, we have used approximately equal ranges of rates of shear.

In all of the determinations low shearing stresses were employed so as to insure the absence of slippage of the samples at the walls of the viscometer.

In table 6 are given the "equilibrium viscosities" of the air-blown as-

TABLE 6
"Equilibrium viscosities" of air-blown asphalts G, H, and I at 25°C.

ASPHALT	MEAN SHEARING STRESS	TIME OF WORKING	TIME FOR ATTAIN- MENT OF EQUILIB- RIUM " η "	RATE OF SHEAR	EQUILIB- RIUM " η "	BREAKDOWN OF STRUCTURE BY CONTINUED WORKING
	<i>dynes per cm.²</i>	<i>minutes</i>	<i>minutes</i>	<i>reciprocal seconds $\times 10^4$</i>	<i>poises $\times 10^{-4}$</i>	
G (65 penetration)...	21,900	1,260	100	1.16	188	None
	43,800	805	615	5.21	84.0	Slight
	76,800	10	*	13.9*	55.2*	Considerable*
	76,800	545	*	30.0*	25.7*	Considerable*
H (94 penetration)...	1,060	400	50-400†	0.434	24.4	None
	2,150	770	40-700†	0.870	24.7	None
	4,340	445	35-425†	1.74	24.9	None
	8,730	690	30-630†	3.77	23.1	None
	32,900	10	*	20.3*	16.2*	Considerable*
	32,900	645	*	38.6*	8.52*	Considerable*
I (132 penetration)...	1,060	260	150-240†	0.231	4.58	None
	4,340	790	50-740†	1.00	4.34	None
	10,900	10	*	27.8*	3.92*	Some*
	10,900	440	*	35.2*	3.09*	Some*

* An equilibrium velocity was not attained during the time allotted to the experiment; the viscosity continued to decrease on further working.

† The time could not be ascertained more accurately because the equilibrium state was attained in the sample during the absence of the observer.

phalts G, H, and I, as measured in the conicylindrical rotation viscometer at 25°C.

At low shearing stresses the samples were worked for long periods of time to make certain that "equilibrium viscosities" had really been attained. It is evident from table 6 that at the lowest stresses none of these asphalts shows thixotropic behavior in this instrument, although they are quasi-viscous (i.e., the "equilibrium viscosity" is dependent on the shearing stress employed). At the highest stress employed in each case, however,

the breakdown of structure is very evident, since the "viscosities" diminish with time at constant shearing stress. These experiments substantiate the results shown in figures 3, 4, and 5 for asphalt F in indicating that there is a critical shearing stress at which the structure of the asphalt sample is broken down to some extent in this instrument with continued working in a given direction. At all stresses above this threshold value thixotropy is manifested.

TABLE 7
"Equilibrium viscosities" of air-blown asphalt G (65 penetration)

TEMPERATURE	MEAN SHEARING STRESS	TIME OF WORKING	TIME FOR ATTAINMENT OF EQUILIBRIUM " η "	RATE OF SHEAR	EQUILIBRIUM " η "	BREAKDOWN OF STRUCTURE BY CONTINUED WORKING
$^{\circ}\text{C.}$	<i>dynes per cm.²</i>	<i>minutes</i>	<i>minutes</i>	<i>reciprocal seconds $\times 10^4$</i>	<i>poises $\times 10^{-8}$</i>	
25 0	21,900	1,260	100	1.16	188	None
	43,800	805	615	5.21	84.0	Slight
	76,800	10	*	13.9*	55.2*	Considerable*
	76,800	545	*	30.0*	25.7*	Considerable*
35 0	1,060	360	300	0.434	24.4	None
	6,530	170	70	2.61	25.0	None
	10,900	970	100-820†	4.19	26.0	Slight
	32,900	10	*	19.7*	16.7*	Considerable*
	32,900	420	*	51.4*	6.40*	Considerable*
45.0	511	840	20	1.00	5.07	None
	1,170	540	320	2.60	4.50	None
	3,240	260	30	6.65	4.87	None
	8,730	10	*	22.0*	3.96*	Some*
	8,730	235	*	29.5*	2.95*	Some*
55.0	504	240	90	6.96	0.724	None
	1,050	130	20	15.0	0.696	None
	2,490	130	30	32.5	0.766	None

* An equilibrium velocity was not attained during the time allotted to the experiment; the viscosity continued to decrease on further working.

† The time could not be ascertained more accurately because the equilibrium state was attained in the sample during the absence of the observer.

If the "equilibrium viscosities" of asphalts G, H, and I are compared at equal ranges of rate of shear, it is noticed that the harder the asphalt (i.e., the more it has been processed), the greater is the deviation from Newtonian flow. This is true even if we omit from this comparison the "equilibrium viscosity" values at the highest stresses, where breakdown of structure causes marked decreases in the "viscosities."

The anomalous flow properties of the blown asphalts G, H, and I were similar to those of the batch steam-refined asphalt F, but more pronounced.

No means has been found for expressing the "degree of deviation" from Newtonian flow as a function of the amount of dispersed phase. In the first place, there is no method of expressing the amount of divergence from purely viscous flow. Secondly, the percentage of asphaltenes is not an absolute measure of the colloidal nature of the asphalt. Although asphaltenes are defined by a solubility test, they vary appreciably in molecular weight and probably in composition for different types of asphalt. Also, the continuous phase (petrolenes) may differ greatly in various asphalts. The natures as well as the amounts of the continuous and dispersed phases are undoubtedly responsible for the colloidal characteristics of asphalts.

INFLUENCE OF TEMPERATURE ON ANOMALOUS FLOW PROPERTIES

As the temperature increases, the high molecular weight constituents of asphalt (asphaltenes) become more soluble in the continuous oily phase (petrolenes), and a gradual transition occurs in the nature of the flow exhibited by the system. With increasing temperature, the elastic and thixotropic properties of the asphalt system, as well as its quasi-viscous character, are less pronounced; at a high enough temperature the system exhibits truly viscous flow. Table 7 presents the "viscosity" data of the air-blown asphalt G at various temperatures. At 55°C. this sample exhibited viscous flow within the range of shear rates used in these experiments. As the temperature was lowered, the anomalous flow properties became more exaggerated. Determinations were made at approximately equal ranges of rate of shear for the reason stated in the previous section.

CONCLUSION

The flow characteristics of asphalts are frequently complex, indicating that their physical structure and chemical composition are exceedingly involved. Some asphalts appear to be truly viscous, whereas others exhibit varying degrees of anomalous flow (thixotropy, age-hardening, quasi-viscousness, and elasticity). The magnitude of these characteristics depends largely on the source of the asphalt, the degree of processing, and the temperatures and rates of shear at which the measurements of flow are made. It is generally believed that the source, processing, and temperature of test influence the nature and amount of dispersed material present (i.e., the colloidal nature of the asphalt). Of course, the rate of shear has a profound influence on the physical structure of the system at the time of measurement. The presence of flow properties which are generally characteristic of colloidal systems lends strong support to the concept that asphalts are distinctly colloidal. In the case of truly viscous asphalts, the change of viscosity with decreasing temperature is continuous and there is no evidence of a sudden change from a sol to a gel condition, or from a semisolid to a solid state, as some workers have erroneously concluded from insufficient data.

The gradual formation of an internal secondary structure unstable to heat and mechanical working has been noted in all types of asphalt, whether viscous or not. This occurrence of age-hardening is another conclusive proof that asphalts are colloidal in nature.

The authors are indebted to Mr. H. E. Schweyer for suggestions and the drawings.

REFERENCES

- (1) Academy of Sciences at Amsterdam. Uitgave van de N.V. Noord Hollandsche Uitgevers-Maatschappij, Amsterdam (1935). "First Report on Viscosity and Plasticity prepared by the Committee for the Study of Viscosity."
- (2) A.S.T.M. Designation D88-33. Am. Soc. Testing Materials Standards Part II, 880 (1933).
- (3) A.S.T.M. Designation D5-25. Am. Soc. Testing Materials Standards Part II, 971 (1933).
- (4) A.S.T.M. Designation D36-26. Am. Soc. Testing Materials Standards Part II, 984 (1933).
- (5) BINGHAM, E. C.: Fluidity and Plasticity. McGraw-Hill Book Co., Inc., New York (1922).
- (6) BINGHAM, E. C., AND MURRAY, H. A.: Proc. Am. Soc. Testing Materials **23**, II, 655 (1923).
- (7) BINGHAM, E. C., AND STEPHENS, R. A.: Physics **5**, 217 (1934).
- (8) BRAUNBEK, W.: Z. Physik **57**, 501 (1921).
- (9) EVANS, E. V., AND PICKARD, H.: An Investigation into the Nature and Properties of Coal Tar. South Metropolitan Gas Co., London (1931).
- (10) EYMANN, W.: Teer u. Bitumen **31**, 165 (1933).
- (11) FERRY, J. D., AND PARKS, G. S.: Physics **6**, 356 (1935).
- (12) International Critical Tables, Vol. I, p. 32. McGraw-Hill Book Co., Inc., New York (1926).
- (13) KLINKMANN, G. H.: Asphalt Teer Strassenbautech. **31**, 942 (1931).
- (14) MACK, C.: J. Phys. Chem. **36**, 2901 (1932).
- (15) MOONEY, M., AND EWART, R. H.: Physics **5**, 350 (1934).
- (16) NELLENSTEYN, F. J.: J. Inst. Petroleum Tech. **10**, 311 (1924).
- (17) NELLENSTEYN, F. J.: J. Inst. Petroleum Tech. **14**, 134 (1928).
- (18) NELLENSTEYN, F. J., AND Roodenburg, N. M.: Kolloid-Beihefte **31**, 434 (1930).
- (19) PITTMAN, C. U., AND TRAXLER, R. N.: Physics **5**, 221 (1934).
- (20) POCHEITINO, A.: Nuovo cemento **8**, 77 (1914).
- (21) RICHARDSON, C.: J. Ind. Eng. Chem. **7**, 463 (1915).
- (22) RODIGER, W.: Kolloid-Z. **66**, 351 (1934).
- (23) SAAL, R. N. J.: Chem. Weekblad **32**, 435 (1935).
- (24) SAAL, R. N. J.: Chem. Weekblad **32**, 486 (1935).
- (25) SCHWEYER, H. F., COOMBS, C. E., AND TRAXLER, R. N.: To appear in Proc. Am. Soc. Testing Materials **36**, II (1936).
- (26) SPIERS, H. M.: Brennstoff-Chem. **9**, 77 (1928).
- (27) TRAXLER, R. N., AND SCHWEYER, H. E.: Physics **7**, 67 (1936).
- (28) TRAXLER, R. N., AND SCHWEYER, H. E.: To appear in Proc. Am. Soc. Testing Materials **36**, II (1936).
- (29) TRAXLER, R. N., AND SCHWEYER, H. E.: To appear in Am. Soc. Testing Materials **36**, II (1936).

PARTICLE SIZE AND OPTICAL PROPERTIES OF EMULSIONS¹

EMERSON D. BAILEY, J. BURTON NICHOLS, AND
ELMER O. KRAEMER

*The Experimental Station of E. I. duPont de Nemours and Co., Inc.,
Wilmington, Delaware*

Received June 11, 1936

Numerous efforts have been made to calculate theoretically the dependence of the light-scattering power of suspensions upon the size and refractive index of the particles, the refractive index of the medium, and the wave length of light used. For infinitely small, non-absorbing particles in a non-absorbing medium, Rayleigh's treatment (9) is generally judged satisfactory, but if the particle size approaches the order of magnitude of the wave length of light, or if the particle is colored, the theoretical calculation of scattering becomes much more difficult and a matter of approximation (1, 4, 5, 6, 8, 9, 11). On the other hand, the empirical correlation of experimental data on light scattering with relevant physical factors has on the whole been unsatisfactory, owing to insufficiently accurate information on particle size. As a rule, investigators have had to be satisfied to assume their suspensions to contain particles of uniform size, although as a matter of fact, any artificial and practically all natural suspensions contain particles of definitely non-uniform size.

Fortunately, the Svedberg ultracentrifuge can under favorable conditions provide the required information, but rather involved calculations are required to extract the desired relations between light scattering and particle size, owing to the fact that the ultracentrifuge does not give directly a particle-size distribution. Specifically, a particle-size distribution may be expressed as a relationship between dc/dr and r , where dc/dr is proportional to the weight of particles having a radius between r and $r + dr$. The ultracentrifuge, however, gives the relation between $d(kc)/dr$ and r , where k is the apparent absorption coefficient of a suspension of particles of radius r . For a suspension of colorless particles in a colorless medium, the "absorption" is of course entirely due to scattering, and the "absorption coefficient" in such cases provides a measure of the light-scattering

¹ Presented at the Thirteenth Colloid Symposium, held at St. Louis, Missouri, June 11-13, 1936.

Contribution No. 172 from the Experimental Station of E. I. duPont de Nemours and Co., Inc.

power of the suspension. The relation between $d(kc)/dr$ and r we call a "weight-optical distribution," and since k in general varies with r , the "weight-optical distribution" normally is not identical with the true "weight distribution" curve (7).

In this paper, a method will be described for calculating, with the aid of a simple mechanical product-integraph, the relationship between the "absorption coefficient" k and the radius from a series of weight-optical distribution curves. In addition, the light-scattering powers of a series of emulsions of constant particle-size distribution but different refractive index relations are reported in terms of apparent absorption coefficient k , and a general relation connecting the apparent absorption coefficient with particle size, the refractive indices of particles and medium, and the wave length is deduced by means of the product-integraph.

THE PRODUCT-INTEGRAPH AND ITS USE

The most direct way of determining the relation between absorption coefficient (as a measure of light scattering) and radius for a certain kind of particle in a medium of specified refractive index is by the analysis of a series of weight-optical distribution curves for suspensions with different particle sizes.

If a given weight-optical distribution be represented by the equation

$$d(kc)/dr = f_n(r)$$

and the variation of the absorption coefficient k with r be represented by

$$1/k = F(r)$$

then, in general, it follows that

$$\int_{r_{\min.}}^{r_{\max.}} f_n(r) \cdot F(r) = 1$$

Each weight-optical distribution is represented by a particular $f(r)$, and our task is to calculate $F(r)$ from the series of simultaneous integral equations equal in number to the experimentally determined weight-optical distributions. Since the solution of such equations with the required accuracy is impractical by algebraic means, a mechanical product-integraph based upon the principles of a two-dimensional moment balance was devised for the purpose.

The moment balance was simply a drawing board supported on a fulcrum and carrying a system of coördinates. The r -axis (or abscissa) coincides with the fulcrum. The $f_n(r)$ functions are divided into a number of equal areas (e.g., 10) and are represented by a series of equal weights (for instance, 10 g. each). Each weight is placed at the mean r value for the area it represents. On the left-hand side of the board, 10 cm. from the

fulcrum, a weight of 100 g., representing unit moment, is placed. On the right-hand side of the board, perpendicular to the fulcrum, $F(r)$ is measured along the ordinates.

When the weights representing any $f(r)$ are placed at their appropriate r -positions and their ordinates adjusted until the board balances, the corresponding equation of the set is satisfied, and $F(r)$ is the curve drawn through the positions of the weights. Each of the experimental functions $f(r)$ is put on the moment balance separately, and $F(r)$ is adjusted until, by a process of trial and error, an $F(r)$ curve is found which will satisfy all of the equations. The resulting curve represents the relation between $1/k$ and radius, which of course can be readily converted, if desired, into a curve of k versus radius. With a moment balance sensitive to differences in moments of 0.3 per cent, an $F(r)$ curve can be found that satisfies the experimental data to 3 to 4 per cent.

A specific example of the use of this product-integral for determining the relationship between "absorption coefficient" and particle radius has previously been presented (3), and a more detailed description of the theory of the product-integral is published elsewhere (2).

THE EFFECT OF REFRACTIVE INDEX AND PARTICLE SIZE UPON ABSORPTION COEFFICIENT (LIGHT SCATTERING)

Inasmuch as the light-scattering efficiency of a particle is affected by particle shape and is complicated by double refraction in solid particles, emulsions were chosen as representing ideal conditions. A stock emulsion of Nujol in 76 per cent glycerol containing 1 per cent of Castile soap was prepared and thoroughly homogenized. From this stock emulsion, a series of emulsions of the same particle-size distribution but with markedly different light-scattering properties was prepared by reduction of the refractive index of the medium by dilution with various proportions of glycerol and water. Six emulsions with the dispersion medium varying from 15 to 76 per cent of glycerol were so prepared, corresponding to a range in refractive index of the medium from 1.359 to 1.444 at a wave length of 444 millimicrons, where the absorptions and weight-optical distributions were measured. At the same wave length, the refractive index of the Nujol is 1.488.

The weight-optical distribution curves of the six emulsions were determined with the Svedberg low-speed ultracentrifuge in the usual manner and are presented in figure 1. The areas of these curves are equal to the light absorptions, measured also in the ultracentrifuge within an aperture of about 4° , with a parallel beam of incident light (see table 1). The "absorption coefficients" are defined in the conventional way and refer to a suspension containing 0.01 cc. of particles per 100 cc. of suspension.

In contrast to the case described above, the $F(r)$ function is different for

each of these emulsions, owing to the differences in the refractive indices, but the function relating concentration and radius (i.e., dc/dr versus r) is the same. It was found that the differences in light-scattering efficiency

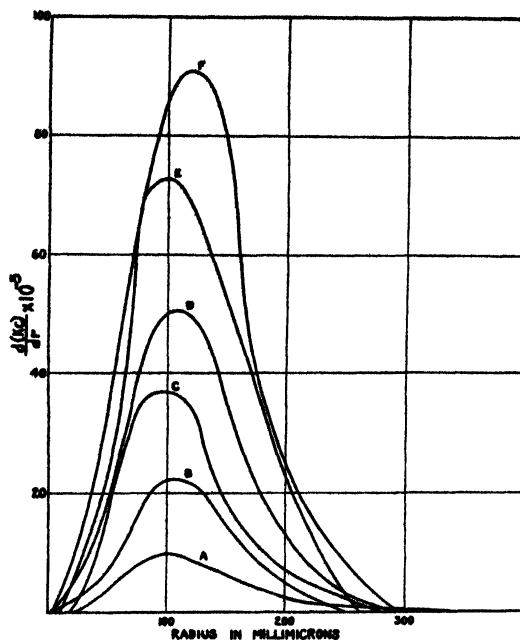


FIG. 1. Weight-optical distribution curves of series of emulsions with the same particle-size distribution but different refractive index of the medium.

TABLE 1
Absorption coefficients of Nujol emulsions

EMULSION	ABSORPTION COEFFICIENT	EMULSION	ABSORPTION COEFFICIENT
NE-2A	0.0293	NE-2D	0.162
-2B	0.0656	-2E	0.236
-2C	0.110	-2F	0.300

as determined by the refractive indices could be reduced to a common denominator, as it were, by use of the dimensionless factor

$$\frac{m^2 - 1}{m^2 + 2} \cdot \frac{n_0}{\lambda} \cdot r$$

where m is the ratio of the refractive index of the particle to that of the medium, n_0 is the refractive index of the medium, λ is the wave length of the light used in vacuum, n_0/λ is therefore the wave length of the light used in the medium, and r is the particle radius. This factor we call the

“relative optical radius.” The abscissa values of the weight-optical curves were converted to a “relative optical radius” basis.

The ordinates of the weight-optical distributions were in turn multiplied by the corresponding radii. The resulting curves (figure 2) could then be treated in the same fashion as the $f(r)$ functions discussed in the section on the product-integrals and its use, and a curve obtained with the prod-

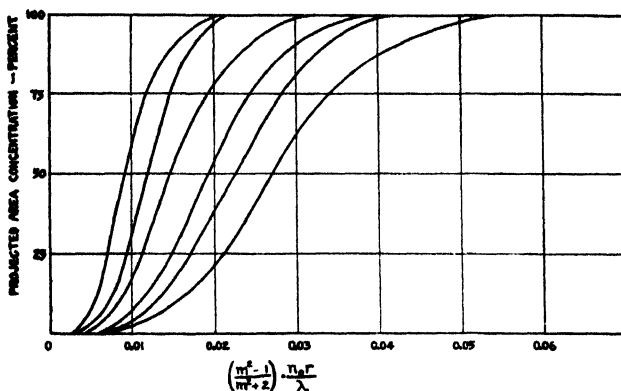


FIG. 2. Projected area concentration in per cent versus relative optical radius

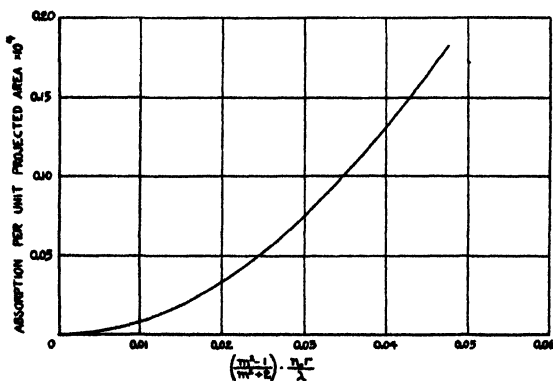


FIG. 3. Generalized curve relating the absorption constant of a suspension with the concentration, particle size, refractive indices of particle and medium, and the wave length.

uct-integrals relating $1/(kr)$ and the “relative optical radius.” Figure 3 presents kr versus “relative optical radius.” k in this case refers to the absolute “absorption coefficient” of a suspension containing 0.01 cc. of particles per 100 cc. of suspension measured under the specified conditions of illumination and angle of collection. kr we refer to as the “absorption coefficient per unit projected area.”

Presumably, figure 3 should describe the light absorption for the indicated range of relative optical radius, regardless of the values of the individual quantities entering into the relative optical radius. Experimentally, however, the actual range in values covered is as follows:

$$\begin{aligned}r &= 20 \text{ to } 270 \text{ m}\mu \\m &= 1.03 \text{ to } 1.94 \\n_0 &= 1.359 \text{ to } 1.444 \\\lambda &= 444 \text{ m}\mu\end{aligned}$$

Further work will be required before we can be sure that the method here employed for correlating the various factors involved is really as generally valid as it now appears.

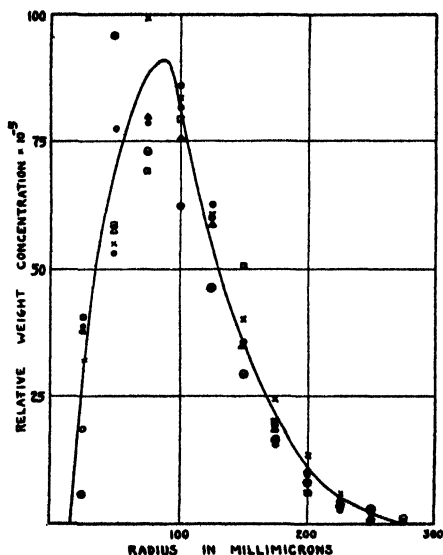


FIG. 4. The weight-distribution curve for the series of emulsions, as calculated from the weight-optical curves of figure 1 and the generalized curve of figure 3.

Figure 4 presents the weight-distribution curves for the emulsions used, as calculated from the experimental weight-optical distribution curves by means of the generalized curve of figure 3.

The relation of these experimental results to theoretical calculations of light scattering will be discussed in a later publication.

REFERENCES

- (1) ANDREEV: J. Gen. Chem. U. S. S. R. **5**, 529 (1935).
- (2) BAILEY: To appear in Rev. Sci. Instruments.

- (3) BAILEY, NICHOLS, AND KRAEMER: Paper presented at the Eighty-eighth Meeting of the American Chemical Society, held in Cleveland, Ohio, September, 1934.
- (4) BLUMER: Z. Physik **32**, 119 (1925); **38**, 304, 920 (1926).
- (5) CASPERSSON: Kolloid-Z. **60**, 151 (1932); **65**, 162 (1933).
- (6) MIE: Ann. Physik [4] **25**, 377 (1908).
- (7) NICHOLS, BAILEY, AND KRAEMER: J. Phys. Chem. **36**, 328 (1932).
- (8) PUTZEYS AND BROSTEAUX: Trans. Faraday Soc. **31**, 1314 (1935).
- (9) RAY: Proc. Indian Assoc. Cultivation Sci. **7**, 1 (1921); **8**, 23 (1923).
- (10) RAYLEIGH: Phil. Mag. [5] **47**, 375 (1899).
- (11) SHOULEJKIN: Phil. Mag. **48**, 2, 307 (1924).



ULTRAFILTRATION THROUGH CELLOPHANE OF POROSITY ADJUSTED BETWEEN COLLOIDAL AND MOLECULAR DIMENSIONS¹

JAMES W. MCBAIN AND R. F. STUEWER

Department of Chemistry, Stanford University, California

Received June 11, 1936

Some years ago we found that the pores of commercial Cellophane swollen in water happened to be of such size that ordinary molecules, such as sucrose or anthracene, passed through freely, while all known colloids were partially or wholly held back (5). Now we find that Cellophane, Sylphrap, and Viscacelle, as at present manufactured, possess distinctly finer pores, so that a portion even of sucrose or potassium chloride is held back on ultrafiltration.

Such cellulose membranes possess the great advantage that they are chemically indifferent and that the same membrane can be used for a series of different solutions or solvents without noticeable change in porosity, provided that the transition from one solvent to another is made by washing through with mutually miscible liquids. Such Cellophane serves as a most useful test to prove the presence or absence of colloidal matter, or as a means of measuring the amount of crystalloid present in the colloidal solution. It was very convenient that unlimited supplies of such uniform material were commercially available, requiring no troublesome laboratory preparation. Naturally, care had to be taken to obtain Cellophane, etc., which had not been waterproofed in any way.

Formerly we were interested in the problem of adjusting the size of pores down to finer and finer molecular dimensions, so as to separate the ordinary large molecules, such as sucrose or potassium chloride, from small molecules, such as methyl alcohol and water. This was readily achieved by deposition of collodion or viscose in the pores by filtering the necessary amount of their solutions through the Cellophane, thus producing molecular sieves of any desired fineness. Cellophane which has not been swollen in water is practically air-tight.

Now that commercial membranes are denser, we are faced with the opposite problem of finding some simple method of restoring them to the invaluable position they formerly occupied, intermediate between ordinary

¹ Presented at the Thirteenth Colloid Symposium, held at St. Louis, Missouri, June 11-13, 1936.

recognized molecules and the finer colloidal particles. In a paper on dyeing Morton (6) reported that the permeability of Viscacelle is greatly increased by a treatment with sodium hydroxide. In the present investigation, we have found that solutions of zinc chloride of particular concentration are most satisfactory for achieving our purpose. We are greatly indebted to the manufacturers of Cellophane, Sylphrap, and Viscacelle for samples and even for a specimen of Cellophane that never had been allowed to dry.

The subject of ultrafiltration is not quite simple: This was well brought out in a valuable and careful study by Ershler (1), who studied the effect of stirring upon the apparent permeability of a collodion membrane.² We have been led to investigate systematically the effects of pressure and of stirring upon the simplest case, that of a non-electrolyte such as sucrose. Other observations refer to the effect of molecular size and of the electrical effects with salt solutions or charged colloidal sols. We have also taken occasion to measure the hydration of pectin.

I. CONTROL OR ADJUSTMENT OF THE POROSITY OF CELLULOSE MEMBRANES

Not only is modern sheet cellulose (Cellophane, etc.) denser than formerly, but, as was pointed out in previous communications, Cellophane swells less after aging, or at higher temperature (3). Freshly manufactured Cellophane may swell as much as threefold in thickness (not in length, nor more than a few per cent in width), but after keeping for several years it may swell to less than double its thickness. The change in thickness goes parallel with change in porosity. Dry No. 300 Cellophane and Sylphrap are 0.0009 in. or 0.023 mm. thick; this was the material chiefly used in the present investigation. No. 600 Cellophane, previously used, filters more slowly. It also retains distinctly (at least three-halves) more solute.

Swelling in water

With a new and an older sample of Cellophane No. 600, the thickness in inches upon swelling in water for fifteen minutes and for twenty-four hours at three different temperatures was as shown in table 1.

With No. 300 Cellophane swollen in water the dimensions were the same at fifteen minutes as after three hours, as shown in table 2. Thus the Cellophane swollen at room temperature very slowly shrinks again at 100°C.

The porosity and the rate of ultrafiltration also depend upon the tem-

² We are in agreement with his main conclusions except for a few sentences in the first two paragraphs of his paper in which, since his membranes were of unsuitable porosity and were, of course, not suitable for distinguishing between molecules and particles, he stated the *non sequitur* that Kistler's coarse ones likewise were not.

perature of swelling in water. Thus, at 200 pounds pressure, when 3 per cent sucrose was filtered through 24 sq. cm. of filter:

CELLOPHANE SWOLLEN AT	RATE OF ULTRAFILTRATION	SUCROSE RETAINED ³
°C.	grams per minute	per cent
25	0.38	13
100	0.22	22.0

Swelling in sodium hydroxide solution

The porosity of membranes swollen in sodium hydroxide is dependent upon both temperature and concentration. In general, an optimum concentration exists for each temperature, the optimum being more pro-

TABLE 1

Swelling of No. 600 Cellophane in water

TREATMENT OF CELLOPHANE	NEW SAMPLE (DRY 0.0016 IN.)		OLD SAMPLE (DRY 0.0015 IN.)	
	15 min.	24 hrs	15 min.	24 hrs.
	inches	inches	inches	inches
Water at 0°C.	0.0035	0.0035	0.0033	0.0034
Water at room temperature.	0.0035	0.0035	0.0032	0.0034
Water at 100°C.	0.0030	0.0030	0.0028	0.0029

TABLE 2

Swelling of No. 300 Cellophane in water

TREATMENT OF CELLOPHANE	DIMENSIONS
Original.	40 x 76 x 0.023 mm.
Water at room temperature (25°C.)	46.5 x 76 x 0.051 mm.
Water at 100°C.	45 x 76 x 0.038 mm.
Water at 100°C., then 2 days at 25°C.	45 x 76 x 0.038 mm.
Room temperature, then 3 hours at 100°C.	45 x 76 x 0.045 mm.

nounced and the swelling greater at low than at high temperatures. Membranes swollen at low temperatures are more permeable than those swollen first at high temperatures and then brought to lower temperatures, although lowering the temperature after the initial swelling does cause an increase.

³ For the method of calculation and definition of per cent sucrose retained, 1 - ϕ , see part II, below. All ultrafiltrations were carried out with the apparatus previously described, similar to that supplied by Vereinigung Göttinger Werke, Göttingen, with electrical stirrer, which was always used except when otherwise mentioned. The interior was silver-plated, and such parts as the stirrer and filter bed were replaced by pure silver. When electrolytes were present, the plated parts were coated with paraffin. Pressures were obtained from a cylinder of nitrogen.

Conversely, swelling initially at low temperatures and then heating causes a decrease, but not of sufficient magnitude to give the same result as is obtained with the reverse procedure.

Membranes swollen in sodium hydroxide have a tendency to become very brittle, especially when the swelling is large, and so are not satisfactory over a wide range of porosity.

Neale (7) has discussed the swelling of viscose cellulose sheets and presents a plausible theory as to the mechanism. The hysteresis effects just pointed out cannot, however, be explained on the basis of osmotic and Donnan effects.

Swelling in zinc chloride solution

Zinc chloride is a remarkable swelling agent in that its effectiveness is almost confined to the range 60 to 65 per cent. Kahlbaum's best grade of anhydrous zinc chloride was employed, and analysis confirmed its purity and freedom from water.

Detail of procedure for swelling in zinc chloride. The membranes were swollen by first pouring enough of the solution into a flat dish to cover the bottom, then putting in the Cellophane, and finally pouring on the remainder of the solution. Sufficient solution was used to cover the membrane completely, and care was exercised to prevent its adhering to the bottom of the dish. This was accomplished by simultaneously tilting and rotating the dish for the first ten minutes. A coating of paraffin on the bottom of the dish is desirable, but not necessary. At the completion of swelling, i.e., after fifteen to twenty minutes, the excess liquid was carefully pipetted off so as to leave the membrane lying flat. Wrinkling of the surface may lead to cracking of the membrane upon removal of the swelling agent. After removal of the excess liquid, water was poured in and the dish was rotated to speed up diffusion. After a few minutes the membrane was removed and washed free from zinc chloride by means of dilute hydrochloric acid. The acid was then washed out with distilled water. Determination of the ash left upon burning the treated membrane indicated that satisfactory removal of zinc had been effected.

Effect of zinc chloride. As criteria of the extent and effectiveness of swelling we have used the thickness, the rate of filtration, and the per cent of sucrose retained when a 3 per cent sucrose solution is filtered through the membrane. Thickness is significant except at the higher concentrations of zinc chloride, where the surface of the membrane tends to slough off in layers and the softening likewise renders the result uncertain. If insufficient time is allowed for swelling, the sloughing may be uneven. Swelling for long periods instead of fifteen minutes increases sloughing. Sylphrap swells more than Cellophane, and its surface remains smooth. Viscacelle swells less and sloughs more than Cellophane. The swelling

increases steadily with lowering of temperature from 40° down to 10°C., but 3°C. is too low for appreciable swelling in fifteen minutes.

Table 3 shows the degree of reproducibility of swelling in particular concentrations of zinc chloride as judged by the rate of flow of water in grams per minute.

TABLE 3

Effect of swelling No. 300 Cellophane in zinc chloride solutions upon the rate of filtration of water at various pressures (pounds per square inch)

CONCENTRATION OF $ZnCl_2$	RATE OF FILTRATION AT PRESSURES OF			
	40 lbs.	80 lbs.	120 lbs.	200 lbs.
<i>per cent</i>				
60		0 267	0 375	0 558
60		0.285	0 397	0.580
63.0	0 467	1 037	1 408	
63 0	0 450	1.009	1 403	
63 8	1 011	1 968	2 850	
63 8	0.698	1 298	1 782	
64.0	2.125	4 31	5 97	
64 0	1.56	3 13	4 24	

TABLE 4

Increase of thickness on swelling

CONCENTRATION OF $ZnCl_2$	THICKNESS OF		
	Cellophane	Sylphrap	Viscabelle
<i>per cent</i>	<i>inches</i>	<i>inches</i>	<i>inches</i>
Original dry	0 0009	0 0009	0 0009
60	0 0030	0 0035	0 0030
61	0 0040 (after use 0 0035)	0 0043	0 0037
62	0 0046	0 0054	0 0045
63	0 0060*	0 0082**	
64	0 0060* (after use 0 0050)	0 0080**	(0 0055)
65	>0 0060		

* Increase in all dimensions; surface slightly roughened.

** Surface still smooth after 15 minutes. However, after 17 hours the surface is sloughed off.

The thickness increases on swelling as shown in table 4. With the membranes swollen in 63 per cent and 64 per cent solution, filtration of a 3 per cent sucrose until two-thirds or three-quarters had passed through left a residue not more concentrated than 3.01, 3.06, and 3.02 per cent, respectively. Likewise, 3 per cent potassium chloride and 3 per cent potassium iodate passed through unaltered, within the error of analysis. The Cellophane swelled distinctly, both in length and breadth. The rate of filtration for Sylphrap was about three-fifths, and for Viscabelle about two-

fifths that for Cellophane, but the pressure relations were similar to those in table 3. The pressure of 200 pounds appears to compact the membranes, so that the rates are no longer proportional to the pressure, either with water or with solutions.

The effect of pressure upon the retention of sucrose as shown in table 5 will be discussed in part II. Figure 1 shows the pressure dependence of the rates for Cellophane taken from table 5.

As is ordinarily the case with gels, the swollen membranes shrink upon drying and do not regain their original porosity. Experiments upon Cellophane which had never been dried in the course of manufacture were run to determine to what extent the structure might be allowed to collapse without this collapse becoming permanent. Accordingly, strips of the Cellophane were weighed, soaked in glycerol solutions of various concentrations, and then dried and reweighed. The glycerol was then washed

TABLE 5

Effect of swelling No. 300 Cellophane in zinc chloride solution upon the rate of filtration (R in grams per minute) and per cent of sucrose retained from 3 per cent sucrose solution

CONCENTRATION OF ZnCl ₂	THICKNESS	PER CENT OF SUCROSE RETAINED AND RATE OF FILTRATION AT PRESSURES OF							
		40 lbs.		80 lbs.		120 lbs.		200 lbs.	
		Per cent	R	Per cent	R	Per cent	R	Per cent	R
<i>per cent</i>	<i>inches</i>								
0	0.0009	4.3	0.06	9.2	0.14	13.7	0.20	14.5	0.35
61	0.0040	3.7	0.17	5.8	0.34	7.1	0.51	7.3	0.65
64	0.0060	0.0	1.14	0.0	2.10	0.0	2.62	0.0	3.24
65		0.0	1.53	0.0	3.12	0.0	3.97	0.0	

out and the strips were weighed, dried, and weighed for a fourth time. The percentages of free space occupied by the glycerol and the percentage of space regained upon reswelling were calculated as follows:

Per cent of space kept filled while dry..	0.0	9.0	20.3	30.3	41.4	51.5
Per cent of space regained on swelling..	36.9	53.3	84.6	94.4	96.0	98.2

It is apparent that essentially complete recovery of the original form results if 30 per cent or more of the free space is filled while dry. This affords a means of preserving membranes of this type, if it is necessary to dry them. They may be kept in glycerol solution for some time without change also. In water decomposition takes place after a few days.

When membranes were soaked in 50 per cent glycerol and then dried, after seven weeks the glycerol was washed out and the membranes were found to have retained at least nine-tenths of the previous rate of filtration and to have recovered from previous higher pressures.

The experiment also shows that the swelling process with zinc chloride probably does not consist merely in a breaking down of the old structure, but in a setting up of a new structure. That is, the gel particles have not been torn apart, owing to strains within the gel, but rather have been allowed to orientate in such a manner as to relieve the stress. Upon washing out the zinc chloride the ability to orientate is lost, and the new orientation becomes the preferred one. Thereafter the tendency is to return to this form after compression.

The advantages of the method of preparing membranes may be briefly stated. Assuming that no new pores are opened, one may conclude that

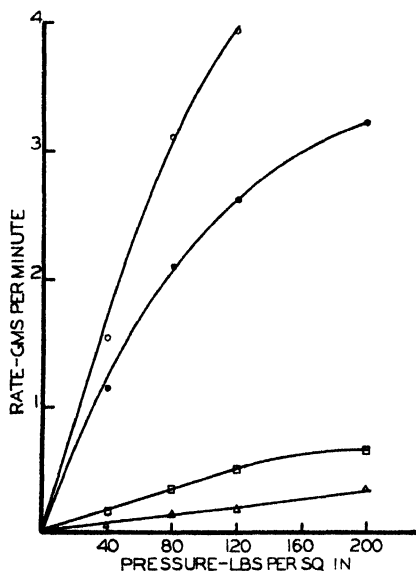


FIG. 1. Effect of zinc chloride on porosity of Cellophane. □, water; △, 61 per cent zinc chloride; ●, 64 per cent zinc chloride; ○, 65 per cent zinc chloride.

in a series of membranes the number of pores and the relative pore sizes may be readily calculated from areas before and after swelling, and from rates of flow of water.

The convenience of the method makes it especially applicable when only a few membranes of varying pore sizes are desired.

II. THE DEPENDENCE OF RETENTION OF ELECTROLYTES AND OF NON-ELECTROLYTES UPON MOLECULAR SIZE, CONCENTRATION, RATE OF STIRRING, PRESSURE, AND OTHER FACTORS

The retention or sieving constant ($1 - \phi$) is defined by Manegold (2) as the constant proportion of solute held back throughout a given filtration,

ϕ being set equal to the ratio between the concentration of original solution and residue for a small amount of filtration. If x_1 and x_2 are the concentrations of successive samples of residue of solution remaining above the filter whose volumes are v_1 and v_2 , it is readily shown that $x_1/x_2 = (v_1/v_2)\phi$, where ϕ is identical with that deduced in Manegold's more complicated expression. Retention will therefore be expressed as $100(1-\phi)$ per cent. In all cases approximately 50 g. was placed in the filter, which had been previously rinsed with several portions of the same solution. After standing a small sample was removed for analysis immediately before filtration began. The residue after filtration was also analyzed.

Effect of size of molecule

Table 6 is of interest in showing how ordinary Cellophane swollen in water discriminates between molecules of progressively larger size. At 350 pounds pressure the rate for the first three was 0.47 g. per minute per 24 cm.²; for raffinose at 200 pounds, 0.35 g.

TABLE 6
Percentage of different molecules held back by ordinary Cellophane

SOLUTE	INITIAL CON- CENTRATION	FINAL CON- CENTRATION	PER CENT RETAINED
	<i>per cent</i>	<i>per cent</i>	
Glycerol (C ₃)	2.96	3.02	2.2
Dextrose (C ₆)	2.86	3.20	7.0
Sucrose (C ₁₂)	2.96	3.53	14.9
Raffinose (C ₁₈)	2.96	3.58	18.1

Effect of concentration, and the contrast between electrolytes and non-electrolytes

Table 7 shows how sucrose compares with a number of electrolytes, and also shows the enormous effect of dilution upon electrolytes first discovered by Ershler for collodion membranes of slightly greater porosity. All these solutions were filtered through the same actual piece of Cellophane at 200 pounds per square inch, except for the viscous 48 per cent sucrose, where 340 pounds were used. The calculation of ϕ is necessarily inaccurate for the dilute potassium iodate, because of the change in ϕ with concentration.

Figure 2 contrasts the relative constancy of retention of sucrose with the great effect of dilution upon an electrolyte such as potassium iodate. Two hundred pounds pressure and the same rate of stirring were used throughout. The most dilute solution of sucrose was 0.05 per cent, where the accuracy of analysis is impaired.

The high retention of very dilute electrolytes is probably due to the charges upon the walls of the pores of the membrane, in accordance with

the principle of Donnan equilibrium,⁴ the effect being suppressed by sufficient concentration of any electrolyte, as is shown at the end of table 7.

TABLE 7

Per cent retained, $100(1 - \phi)$, for a series of solutions filtered through the same piece of Cellophane

DATE	RATE	SOLUTION	PER CENT RETAINED
December 7, 1935	0.39	2.94% KCl	1.92
December 7, 1935	0.38	3.01% KIO ₃	1.78
December 14, 1935	0.33	3.01% sucrose	14.50
December 14, 1935	0.37	6.97% KIO ₃	3.66
December 24, 1935	0.35	0.083% KIO ₃	48.
December 24, 1935	0.35	0.92% CdI ₂	3.45
December 24, 1935	0.29	24.3% CdI ₂	7.55
December 26, 1935	0.31	5.30% NaIO ₃	4.68
December 27, 1935	0.043	48.23% sucrose	8.59
January 7, 1936	0.27	2.99% HIO ₃	5.54
January 18, 1936	0.27	3.01% sucrose	14.16
January 22, 1936	0.27	2.94% KCl	3.57
January 23, 1936	0.29	2.97% KIO ₃	4.5
Another specimen.....		0.087% KIO ₃ + 0.74% NaCl	7.1
Another specimen.....		3.0% NaIO ₃ + 10% NaCl	6.1
Another specimen.....		17.7% KCl	0.9

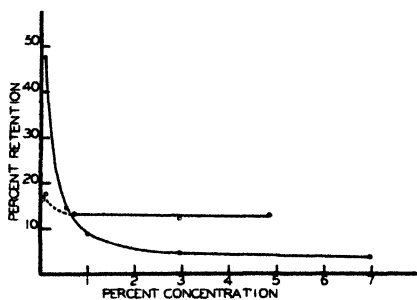


FIG. 2

FIG. 2. Dependence of retention on solute concentration. ○, sucrose; ●, potassium iodate.

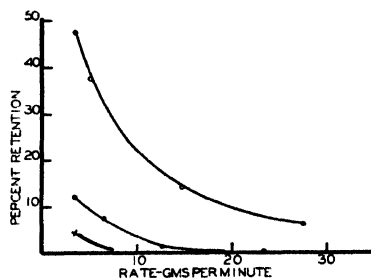


FIG. 3

FIG. 3. Dependence of retention on porosity; retention of sucrose and of potassium iodate of two concentrations by membranes of different porosities. ●, 3 per cent sucrose; ○, 0.08 per cent potassium iodate; ×, 3 per cent potassium iodate.

The effect of the charge in keeping dilute electrolytes away and thus simulating a reduced size of pore may be compared with the similar effect in

⁴ Other influences of Donnan distribution in ultrafiltration were pointed out and discussed by J. W. McBain and W. McClatchie (*J. Am. Chem. Soc.* **55**, 1315 (1933)). For its suppression see reference 3.

dyeing. If so, the rôle of added salt in dyeing is not that of a dispersing agent, as has often been suggested, but rather that the effective pore size is restored.

Effect of varying porosity on retention

Figure 3 exhibits for sucrose and potassium iodate the effect of steadily increasing porosity, as measured by rate of flow at 200 pounds and 140 R.P.M., in permitting more and more complete passage of the solute. It is evident that long after sucrose is passing completely, there is still a marked effect upon the very dilute potassium iodate. For higher ionic concentration the potassium iodate curve lies wholly below that of sucrose. In other words, the exaggerated effect in the dilute electrolyte is a Donnan effect.

Use of membranes for detecting presence of colloid

The data in this paper clearly show that membranes must be suitably chosen and employed if they are to detect and measure the presence of colloid with certainty. It must be shown that the particular membrane is sufficiently porous to pass quantitatively all ordinary molecules, including electrolytes in which the ionic concentration is sufficiently high to suppress Donnan effects. In a previous communication (4) it was concluded that nearly saturated solutions of sodium and potassium iodates contained a distinct proportion of colloid. However, reëxamination of the original records shows that the experiments assembled in that communication were spread over a series of years, and that although the original Cellophane was indeed tested for its complete permeability to electrolytes and non-electrolytes, the much later experiments on the iodates had been carried out with a later and evidently much denser sample of Cellophane. There therefore remains no definite evidence for the presence of appreciable colloid in these solutions, although it may be significant that the retention of cadmium iodide in concentrated solution is twice that in more dilute solution.

Effect of pressure and rate of stirring

Ershler has convincingly pointed out that complete absence of stirring must soon suppress all minor differences between the composition of filtrate and original solution, because of the automatic building up of the compensatingly high concentration in the layer of liquid resting upon the upper surface of the filter.

We extend this to point out in the data here deduced that it is always a race between the rate at which the solution is being bodily thrust through and the rate at which any molecule or particle which cannot freely pass through all portions of the membrane is escaping from its neighborhood,

through electrical influences (Donnan effect), through diffusion, and through convection. Hence, the higher the pressure and the higher the viscosity, and the higher the molecular weight, the greater must be the rate of stirring in order to allow the membrane to exhibit its selective action. Even for a non-electrolyte such as sucrose, these effects are intriguing, as is shown in figure 4. It is quite clear that unless the pores are large enough to pass all similar molecules freely ($1 - \phi = 0$), great care must be taken in interpreting quantitatively the retentions observed under the actual conditions of the filtration.

In figure 4 it is evident that maximum retention occurs when the pressure is 200 pounds per square inch (rate of filtration is 0.44 g. per minute) at the fastest practicable rate of stirring, a rate faster than that for which

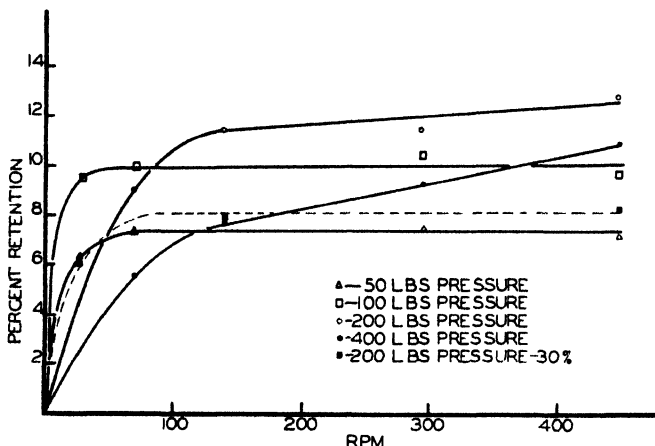


FIG. 4. Dependence of retention on pressure and rate of stirring; percentage of sucrose retained in filtration through ordinary Cellophane at various pressures and rates of stirring. Full lines refer to 3 per cent sucrose; the dashed line to 30 per cent sucrose at 200 pounds pressure.

the instrument is commercially supplied. The position of the curve for 30 per cent sucrose is predictable from the ratio of viscosities or of rates of filtration when compared with 3 per cent sucrose, except at the lowest rate of stirring. Some of the effects are similar to those discussed in the theory of dependence of heterogeneous reaction upon rate of stirring.

SUMMARY

1. Commercial sheet cellulose is much less porous than formerly. It is now necessary to swell in zinc chloride solutions exceeding 63 per cent zinc chloride (37 per cent water), in order to make these membranes freely permeable to all ordinary molecules. Further, the ionic concentration must be sufficient to suppress Donnan effects in the case of very dilute electro-

lytes, including colloids. Contrary to a previous intimation, owing to this change in a commercial membrane there remains no certain evidence for colloid in iodate solutions, although some is indicated in very concentrated aqueous cadmium iodide.

2. With incompletely permeable membranes such as ordinary cellulose, interesting influences of size of molecule, concentration, rate of stirring, pressure, viscosity, and diffusion are observed.

REFERENCES

- (1) ERSHLER, B.: *Kolloid-Z.* **66**, 289 (1934).
- (2) MANEGOLD, E., AND HOFMANN, R.: *Kolloid-Z.* **51**, 221 (1930).
- (3) MCBAIN, KAWAKAMI, AND LUCAS: *J. Am. Chem. Soc.* **55**, 2768 (1933).
- (4) MCBAIN, J. W., AND KISTLER, S. S.: *J. Phys. Chem.* **35**, 130 (1931).
- (5) MCBAIN AND KISTLER: *J. Gen. Physiol.* **12**, 187-200 (1928); *J. Phys. Chem.* **33**, 1806-12 (1929); **35**, 130-6 (1931); *Trans. Faraday Soc.* No. 107, **26**, Part 4 (1930).
- MCBAIN, KAWAKAMI, AND LUCAS: *J. Am. Chem. Soc.* **55**, 2762 (1933).
- (6) MORTON, T. H.: *Trans. Faraday Soc.* **31**, 262 (1935).
- (7) NEALE, S. M.: *J. Textile Inst.* **20**, 373T (1928).

STUDIES IN THIXOTROPY. I

DEVELOPMENT OF A NEW METHOD FOR MEASURING PARTICLE-SIZE DISTRIBUTION IN COLLOIDAL SYSTEMS¹

E. A. HAUSER AND C. E. REED

*Department of Chemical Engineering, Massachusetts Institute of Technology,
Cambridge, Massachusetts*

Received June 11, 1936

INTRODUCTION

In spite of their wide occurrence throughout colloid chemistry, calling forth many investigations, our knowledge of the mechanism of sol-gel transformations and of the structure of the gel state may be described as very rudimentary. This is particularly true in the case of the isothermal reversible sol-gel transformation known as thixotropy.

Thixotropy was first formally observed in iron oxide sols (17), but it has since been reported in many of the hydrous oxide sols as well as in systems as diverse as clay suspensions and heather honey.

For a complete exposition in English of the work on thixotropy we refer the reader to a recent comprehensive monograph by Freundlich (3). Pryce-Jones (11) offers a much shorter review in connection with his studies on the thixotropy of paint.

The characteristic property of a thixotropic system is an increase in its viscosity with time, immediately following mechanical action upon it, all other conditions being constant. Loosely speaking, as long as the system retains those properties ordinarily ascribed to a liquid, it is considered a sol and when it becomes more or less rigid, owing to its constantly increasing viscosity, it is termed a gel. The exact meaning to be attached to the terms "sol" and "gel" will be discussed in a future paper in this series.

Since this isothermal transition from sol to gel appears to be continuous, and since the only difference found to date between sol and gel is mechanical, it is reasonable to conclude that during the period of gelation some type of structure with mechanical resistance to shear is being built up out of the constituent particles of the sol. This picture would postulate a two-phase system, but the type of structure and its mode of formation are subject to discussion.

¹ Presented at the Thirteenth Colloid Symposium, held at St. Louis, Missouri, June 11-13, 1936.

Despite the fact that the chief difference between sol and gel is mechanical and is due to the formation of a structure of some kind out of the constituent particles, there has as yet been no systematic investigation of the effect of particle size upon thixotropy. The importance of this variable has been recognized by Freundlich (3), Russell (12), and Bradfield (1). In idealized form, an investigation of the effect of particle size upon thixotropy should start with a polydispersed system which exhibits the phenomenon, separate the particles into several fractions depending upon their size, and determine the velocity of the sol-gel transformation upon each particle-size fraction at various values of concentration of the dispersed phase, concentration of electrolyte, pH, temperature, etc. The results should be of importance in furthering our interpretation of the mechanism involved and in picturing the final structure. It is the purpose of the present series of articles to describe such an investigation.

The system chosen should first of all exhibit thixotropy to a high degree, exist over a suitable range of particle sizes, and be very stable and reversible, showing a minimum of aging effects. No other system meets these requirements to the same remarkable extent as the clay mineral bentonite of the Wyoming variety.

It became apparent at the start that the initial phase of the investigation would have to concern itself with the development of a rational method for separating a polydispersed system into various particle-size fractions and in turn measuring the distribution of particle sizes in each of these fractions, since no satisfactory method is available at present for such a fractionation in the colloidal range. The remainder of the present paper will describe the method which has been developed for this purpose, and following papers in the series will disclose experimental results and discuss their significance to thixotropy and gel structure in general.

PREVIOUS MEASUREMENT OF PARTICLE-SIZE DISTRIBUTION CURVES

Although a dozen or more methods may be used to determine absolute particle size in a polydispersed system (4), sedimentation rate and sedimentation equilibrium methods are the only ones known for determining the form and value of the particle-size distribution function in a given suspension.

Odén (10) gives the most elaborate description of sedimentation methods. Unfortunately these become increasingly difficult to employ as the dispersed phase approaches colloidal size. Svedberg and Estrup (15) measured particle-size distribution directly in the ultramicroscope by noting rates of fall, but such a method is tedious and needs the questionable assumption that all particles are visible. Westgren (18) combined sedimentation rate with sedimentation equilibrium and presented distribution curves on gold sols, but his measurements were complicated by unavoid-

able diffusion effects. The basket-type centrifuge used by Marshall (7) to determine distribution curves by essentially the same procedure used in gravity fields cannot exert a strong enough field to settle colloidal particles with equivalent spherical diameters of less than 100 μ .

Ultracentrifugal methods as developed by Svedberg and associates (16) are probably the best methods in use at the present time for determination of the distribution function by sedimentation rate or sedimentation equilibrium methods. Unfortunately, the equipment is complicated and so expensive that at present it is enjoyed by but few laboratories in the whole world. A further disadvantage of the ultracentrifuge in the present instance is that it possesses no capacity for making fractionations upon a large quantity of material. McBain (8) has recently been developing the air-driven spinning top as an ultracentrifuge, but while this device is less expensive than a Svedberg machine, it appears to possess no capacity for fractionations.

Of all standard centrifuges on the market the so-called supercentrifuge alone possesses the ability to settle out the finest particles in colloidal sols. Although the supercentrifuge has been used before in colloidal research in clays, notably by Moore, Fry, and Middleton (9) and Bradfield (2), it has never been adapted to the quantitative measurement of distribution curves. Lenoir (6) investigated the use of a laboratory supercentrifuge of the Sharples type for this purpose. The Sharples machine is reasonably priced, and if a technique of evaluating the distribution function by its use could be developed, a valuable tool would be available to many workers. A further advantage of the supercentrifuge in the present instance is its adaptability to fractionations. Lenoir's results indicated that the supercentrifuge had possibilities, but, owing to certain theoretical objections to his calculations, his distribution curves are only of relative significance. While retaining the essential features of the Lenoir experimental technique, the present authors have developed a new method of calculation.

DEVELOPMENT OF THEORY UNDERLYING THE USE OF THE SUPERCENTRIFUGE IN DETERMINING DISTRIBUTION CURVES

The most convenient method for describing a polydispersed system of spherical particles is that proposed by Odén (10). In a given weight of sol let there be T grams of dispersed phase. Since these T grams consist of a great many sizes we can in general plot a curve of percentage of total weight (P) of particles of size below a given diameter (D) against that diameter. Figure 1 represents a system, the largest particle of which is $D_{\max.}$, 100 per cent of the total weight of dispersed phase being below this diameter. It is often more convenient to represent the system by a curve obtained by plotting a new function $f(D)$ against D where $f(D)$ is defined as dP/dD obtained as the slope of the curve in figure 1. Figure 2 represents the same

system as figure 1, with the distribution function dP/dD plotted against D . The area under this curve on figure 2 between D_1 and D_2 represents the percentage of a given weight of dispersed phase having diameters between D_1 and D_2 . The differential percentage of total weight having a given diameter D is $\left(\frac{dP}{dD}\right) dD$ taken at the value of D in question, and the

weight of particles having a given diameter D is $T\left(\frac{dP}{dD}\right) \frac{dD}{100}$. In dealing with anisotropic particles such as are met in the case of clays, the concept of "equivalent spherical radius" must be employed. The geometric significance of this equivalent spherical radius has been described for the important case of discs by L. Squires and W. Squires (13), and found to be a function of the diameter and thickness of the disc. The significance of this anisotropy in the present work will be discussed in a later article.

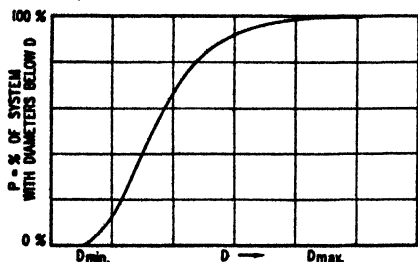


FIG. 1

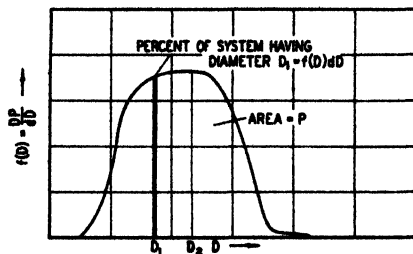


FIG. 2

FIG. 1. Representation of a system, the largest particle of which is D_{\max} , 100 per cent of the total weight of dispersed phase being below this diameter.

FIG. 2. Representation of the same system as in figure 1, with the distribution function dP/dD plotted against D .

The supercentrifuge consists of a balanced vertical bowl coupled to an electric motor drive. Figure 3 is a schematic cross section of the bowl, emphasizing the essentials of the flow. The suspension is fed into the rapidly rotating bowl at the point marked "liquid feed". It then passes two straightening vanes at right angles to each other and flows up the sides of the bowl in a film and out of the bowl over the edge of the weir marked "exit". The thickness of the film on the walls is determined by the diameter of the weir at the top.

Under the influence of centrifugal force the particles settle out onto the walls of the bowl, which are covered with a removable celluloid liner. When a convenient amount of suspension has flowed through the bowl, the feed is cut off and the liner removed. The settled particles are scraped off at definite distances up the bowl and weighed. From these data, and knowing the rate at which the suspension was fed, the rotational velocity

of the bowl, the temperature, the densities of the dispersed phase and dispersing medium, and the dimensions of the bowl, the distribution curve for the suspension is calculated.

Figure 3 also shows the path of settling of the particle. In general this will be a curve, since the particle has a velocity parallel to the axis of rotation due to the flow through the bowl and a velocity perpendicular to the axis of rotation due to the centrifugal force. Any particle p of diameter D starting to settle at a distance of X_0 from the axis of rotation will come to rest upon the wall of the bowl at some definite point A at a distance y from

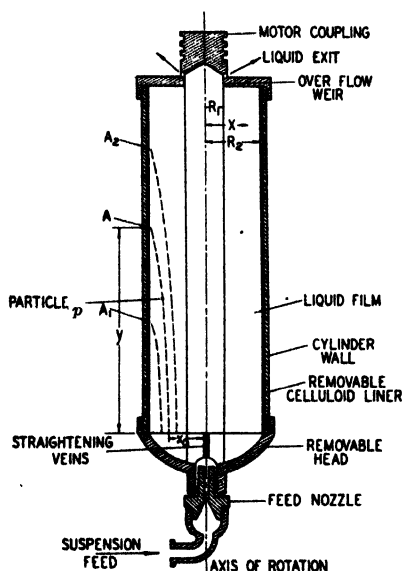


FIG. 3. Section through supercentrifuge cylinder

the entrance. Under constant settling conditions (temperature, angular velocity of bowl, rate of feed) the relation between X_0 , y , and D is definite and may be expressed as

$$F(X_0, y, D) = 0 \quad (1)$$

or

$$X_0 = \phi(y, D) \quad (2)$$

It is important to note that any particle similar to p starting to settle at some larger value of X_0 (i.e., at a point nearer the wall) will settle out on the wall at some point A_1 before point A is reached. On the other hand, a particle similar to p starting to settle at a smaller value of X_0 will come to rest at some point A_2 beyond A .

If the suspension contains a number of particles, N_D , similar to p flow-

ing into the bowl, and if we consider the suspension uniformly mixed at the time settling begins, the number of these particles N'_D which have settled out onto the wall before point A is reached is given by the product of N_D and the ratio of the total volume of suspension flowing across the area enclosed by the concentric circles of radii X_0 and R_2 to the total amount of suspension fed into the bowl.

$$N'_D = N_D \frac{\int_{X_0}^{R_2} u dA}{Q} = N_D \frac{\int_{X_0}^{R_2} u 2\pi X_0 dX_0}{Q} \quad (3)$$

A = cross-sectional area of film in square centimeters,

u = local velocity of flow parallel to the axis of rotation at any point X_0 in the film in centimeters per second,

Q = volumetric rate of feed in cubic centimeters per second, and

R_2 = radius of the bowl less the thickness of the celluloid liner.

The weight of the particles settled out is proportional to their number so that

$$W'_D = W_D \frac{\int_{X_0}^{R_2} u 2\pi X_0 dX_0}{Q} \quad (4)$$

where W'_D is the weight of particles similar to p which have settled out onto the wall and W_D is the total weight of particles similar to p which have flowed into the bowl.

Consider now feeding into the centrifuge T grams of a polydispersed system the distribution function of which is known. Then up to any point, y , on the liner, that portion of the cumulative weight due to particles of diameter D similar to p which have settled out will be:

$$W'_D = T \left[\frac{\int_{X_0}^{R_2} u 2\pi X_0 dX_0}{Q} \right] \left(\frac{dP}{dD} \right) \frac{dD}{100} \quad (5)$$

The total weight due to particles of all diameters settled out up to a point y will be denoted by $W_{(y)}$ and is equal to the sum of the W_D terms due to every particle size.

$$W_{(y)} = \sum_{D=D_{\min.}}^{D=D_{\max.}} W'_D = T \sum_{D=D_{\min.}}^{D=D_{\max.}} \left[\frac{\int_{X_0}^{R_2} u 2\pi X_0 dX_0}{Q} \right] \left(\frac{dP}{dD} \right) \frac{dD}{100} \quad (6)$$

The summation can be expressed as a definite integral.

$$W_{(y)} = T \int_{D=D_{\min.}}^{D=D_{\max.}} \left[\frac{\int_{X_0}^{R_2} u 2\pi X_0 dX_0}{Q} \right] \frac{f(D)}{100} dD \quad (7)$$

In this equation X_0 is calculated as a function of D at any value of y by equation 2.

Having obtained experimentally values of W at various values of y , knowing u as a function of X_0 , and knowing the form of ϕ in equation 2, we can establish the form of $f(D)$ from this integral equation.

To simplify the first calculations it was decided to neglect the effect of variation in the local velocity of flow of the suspension over the cross section of the film at the entrance to the bowl, but to take this into account when considering the settling path of the particles.

As equation 3 stands it is perfectly general and would apply to any kind of a velocity gradient found in the film. With the simplification mentioned N'_D will be given by the product of N_D and the ratio of the area enclosed by the concentric circles of radii X_0 and R_2 to the total cross-sectional area of the film. It may be seen that the result expressed in equation 8 is equivalent to assuming that at the entrance to the bowl where settling starts a constant amount of dispersed phase flows across every increment of area. Under these conditions equation 3 reduces to:

$$N'_D = N_D \left[\frac{R_2^2 - X_0^2}{R_2^2 - R_1^2} \right] \quad (8)$$

where R_1 = inner radius of liquid film. Where equation 7 reduces to:

$$W_{(y)} = T \int_{D=D_{\min.}}^{D=D_{\max}} \left[\frac{R_2^2 - X_0^2}{R_2^2 - R_1^2} \right] \left[\frac{f(D)}{100} \right] dD \quad (9)$$

No success was experienced in trying to obtain $f(D)$ from this equation in an analytically rigorous manner, the necessary transformation being unknown to mathematicians. Fortunately the form of solution may be approximated to any desired degree of accuracy. Assume that the suspension is made up of particles of diameters $D_1, D_2, D_3 \dots D_n$, each of fractional amounts $F_1 + F_2 + F_3 + \dots F_n = 1$. Then at any value of y , for example y_1 , we know $W_{(y)}$ and can evaluate $\phi(y, D)$ for every value of D . $W(y)$ may be taken at n different values of y because there are n different diameters $D_1, D_2, \dots D_n$. Thus we have at all values of y

$$\begin{aligned} \frac{W_{(y_1)}}{T} = & \left[\frac{R_2^2 - \phi^2(y_1, D_1)}{R_2^2 - R_1^2} \right] F_1 + \left[\frac{R_2^2 - \phi^2(y_1, D_2)}{R_2^2 - R_1^2} \right] F_2 \\ & + \dots \left[\frac{R_2^2 - \phi^2(y_1, D_n)}{R_2^2 - R_1^2} \right] F_n \end{aligned} \quad (10)$$

$$\begin{aligned}
 \frac{W_{(y_1)}}{T} &= \left[\frac{R_2^2 - \phi^2(y_1, D_1)}{R_2^2 - R_1^2} \right] F_1 + \left[\frac{R_2^2 - \phi^2(y_1, D_2)}{R_2^2 - R_1^2} \right] F_2 \\
 &\quad \vdots \\
 &\quad + \dots \left[\frac{R_2^2 - \phi^2(y_1, D_n)}{R_2^2 - R_1^2} \right] F_n \\
 &\quad \vdots \\
 \frac{W_{(y_n)}}{T} &= \left[\frac{R_2^2 - \phi^2(y_n, D_1)}{R_2^2 - R_1^2} \right] F_1 + \left[\frac{R_2^2 - \phi^2(y_n, D_2)}{R_2^2 - R_1^2} \right] F_2 \\
 &\quad + \dots \left[\frac{R_2^2 - \phi^2(y_n, D_n)}{R_2^2 - R_1^2} \right] F_n
 \end{aligned}$$

The unknowns in this set of n simultaneous equations in n unknowns are the fractional values which can be determined, F_1, F_2, F_3 , etc. Knowing the fractional amounts of all particles present we can plot a curve similar to figure 1 and from it determine the distribution function. In practice it is possible to get a first approximation to the true value of the distribution function by considering the system as being composed of some small number of particles, for example, five. The set of five equations which can then be written can be solved for the fractional amounts of each of the particles and figures 1 and 2 constructed. The form of the distribution function is then varied until it gives values of W at every value of y corresponding to the experimental data. If the form of $f(D)$ is known, W at any value of y is calculated from equation 7 by graphically evaluating the corresponding line integral over all values of D .

To evaluate W at any value of y by this method of graphical integration, it is necessary to plot values of the quantity

$$\left[\frac{R_2^2 - \phi^2(y, D)}{R_2^2 - R_1^2} \right] \frac{f(D)}{100}$$

against D for all values of D . The area under this curve is proportional to W at the value of y in question.

It is recognized that the solution proposed is in fact one of successive approximation. Assumption of the suspension's being composed of a small number of different particles and solution of the corresponding equations simply provides a rational method of making a first approximation as to the form of $f(D)$. The labor involved in solution of the above integral equation may be considerably shortened if a proper integrating machine is available.

It remains now to show how the form of the function ϕ is derived. The necessity for and physical meaning of the equation $X_0 = \phi(y, D)$ has been discussed above. Before the form of the equation may be determined, we must know the nature of the velocity components of a settling particle both parallel to and perpendicular to the axis of rotation.

It is first necessary to establish the type of flow of the suspension itself through the centrifuge. The film of liquid suspension moves up the walls of the bowl by virtue of the hydrostatic head, due to the fact that the film is slightly thicker at the bottom than at the top. At the high speeds of rotation and low rate of feed, it can be shown that this difference is negligible and that no great error will result if the suspension is considered to flow up the walls of the bowl in stream-line flow with the stream lines parallel to the axis of rotation. On this basis it is possible to describe the velocity component parallel to the axis of rotation of a particle settling at any distance from the axis of rotation. The derivation follows that of Lamb (5) with the exception that the boundary conditions for integration are those of a concentric film of fluid rather than a solid tube of fluid. The final equation is

$$\frac{dy}{dt} = VK_1 \left[R_1^2 \ln \frac{X}{R_2} + \frac{R_2^2 - X^2}{2} \right] = u \quad (11)$$

In this equation dy/dt is the velocity parallel to the axis of rotation at any distance X from the axis of rotation. V is the average velocity over the cross section of the entire film calculated from the relation

$$V = \frac{Q}{(R_2^2 - R_1^2)\pi} \quad (12)$$

where Q is the volumetric rate of feed.

K_1 is a function of the construction of the bowl and is given by:

$$K_1 = \frac{R_2^2 - R_1^2}{\frac{3R_1^4}{4} + \frac{R_2^4}{4} - R_2^2 R_1^2 - R_1^4 \ln \frac{R_1}{R_2}} \quad (13)$$

It is recognized that this idealized picture of the flow may be complicated by end effects in the bowl used in the present work, where the ratio of length to diameter was about 10. An experiment was performed to see the magnitude of these end effects.

Essentially, the experiment consisted in filling the centrifuge bowl with salt solution and at a definite time starting to feed in at a definite rate sodium hydroxide solution of the same density and of known normality. Samples of the effluent were taken at various times and titrated with standard hydrochloric acid to determine their sodium hydroxide content. A curve of total equivalents of sodium hydroxide flowing out versus time was then plotted and compared with the theoretical curve calculated on the basis of the above velocity distribution. The results indicated good agreement between theory and experiment.

By designing a centrifuge bowl especially for this work, such errors could be eliminated still further.

The velocity component perpendicular to the axis of rotation is given by Stokes' law (14):

$$\frac{dX}{dt} = \frac{D^2 \Delta \rho \omega^2 X}{18\eta} \quad (14)$$

where $\Delta \rho$ is the difference in density between dispersed phase and dispersing medium, ω is the angular velocity of rotation, and η is the viscosity of the dispersion medium at the temperature of settling.

Dividing equation 11 by equation 14 we obtain the slope of the settling curve for any particle at any point. We obtain:

$$\frac{dy}{dX} = \frac{18\eta VK_1}{D^2 \Delta \rho \omega^2 X} \left[R_1^2 \ln \frac{X}{R_2} + \frac{R_2^2 - X^2}{2} \right] \quad (15)$$

During any one run at constant values of η , V , and ω , we may integrate this equation for any value of D between the limits:

$$\begin{aligned} y &= 0 & X &= X_0 \\ y &= y & X &= R_2 \end{aligned}$$

since the particle has just come to rest upon the wall at some point y .

Integration gives:

$$y = \frac{18\eta VK_1}{\omega^2 \Delta \rho D^2} \left[\frac{R_2^2}{2} \ln \frac{R_2}{X_0} - \frac{R_1^2}{2} \left(\ln \frac{R_2}{X_0} \right)^2 + \frac{X_0^2 - R_2^2}{4} \right] \quad (16)$$

If the rate of feed, temperature, and velocity of rotation are kept constant, this equation is of the form

$$X_0 = \phi(y, D) \quad (2)$$

but is unfortunately implicit in X_0 , for which we wish to solve. Solution of equation 16 for X_0 may be accomplished either through a family of curves or by representation on an alignment chart.

An error in equation 16 arises in the variation of the term R_2 , owing to a layer of particles building up on the wall. This is minimized by using only a small amount of suspension in any one run and thus building up a relatively thin layer of particles. The average deviation of R_2 from its value represented by the diameter of the bowl less the thickness of the removable liner is very slight.

The method which has just been described is well suited for making a particle-size fractionation upon a polydispersed system like bentonite and measuring the distribution curves of the resulting fractions.

The solid line in figure 4 represents the experimental data in a run upon a sample of bentonite from which all large particles had been removed by gravity settling over a period of three months. The distribution curve

calculated from these data is shown as the solid curve in figure 5. The rate of feed was held constant during the run to a value of 7.5 cc. per minute by a constant-level siphon. A total of 282 cc. of suspension of concentration 0.46 per cent were fed through, followed by 300 cc. of distilled water. The centrifuge was operated at a speed of 20,200 R.P.M. ($\omega = 2115$ radians per second) measured by a stroboscope. Speed control was by voltage regulation and the temperature was 21.5°C ., corresponding to a viscosity of water of 0.009695 poise. The density of the bentonite was determined by a pyknometric method as 2.8. This figure, however, is subject to

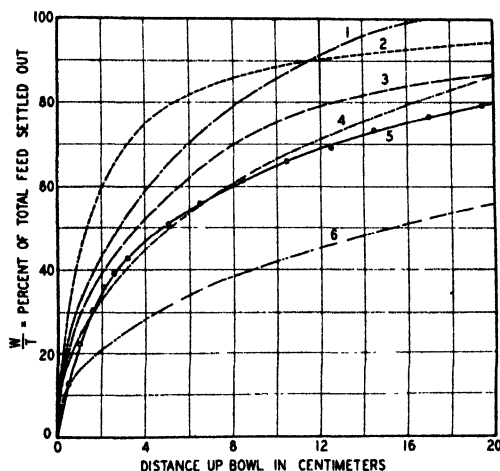


Fig. 4. Data used in calculating distribution curves

1. — — — monodispersed system; $D = 35\text{m}\mu$.
2. - - - - - polydispersed system isodistributed between $D = 12.5\text{m}\mu$ and $D = 90\text{m}\mu$; $f(D) = 1.29 \times 10^6$.
3. — — — polydispersed system isodistributed between $D = 12.5\text{m}\mu$ and $D = 48.8\text{m}\mu$; $f(D) = 2.75 \times 10^6$.
4. — — — monodispersed system; $D = 25\text{m}\mu$.
5. — — — experimental curve; run No. 4.
6. — — — monodispersed system; $D = 15\text{m}\mu$.

revision, as work is in progress to determine the density under settling conditions more accurately. In the present machine $R_1 = 1.07\text{ cm.}$ and $R_2 = 2.117\text{ cm.}$

At the conclusion of the run the liner was removed from the bowl and the precipitate allowed to dry. The precipitated clay was then scraped off at definite distances from the bottom of the liner, dried in an oven, and weighed in ground glass stoppered weighing bottles. Curve 5 of figure 4 was plotted from these data.

The condition imposed upon the distribution function calculated from these data is that integration of equation 7 over all values of D at any value

of y , for example y_1 , must give the experimentally determined value of W , that is W_1 , at y_1 . Figure 6 shows such a graphical integration at the point $y = 10$ cm. The area under the curve is proportional to the total weight of particles $W(y)$ which settled out on the liner up to $y = 10$ cm. The proportionality factor is T , the total weight of dispersed phase fed into the machine during the run (see equation 7).

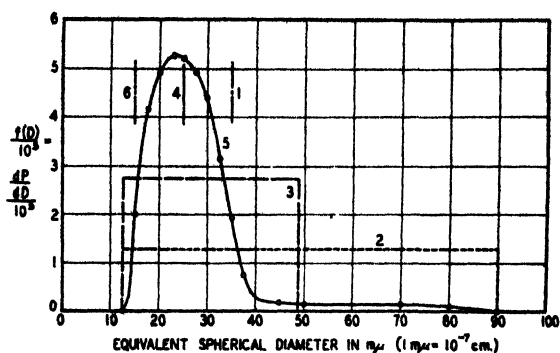


FIG. 5. Distribution curve calculated from curves of figure 4. P = per cent of sample by weight having diameters below D .

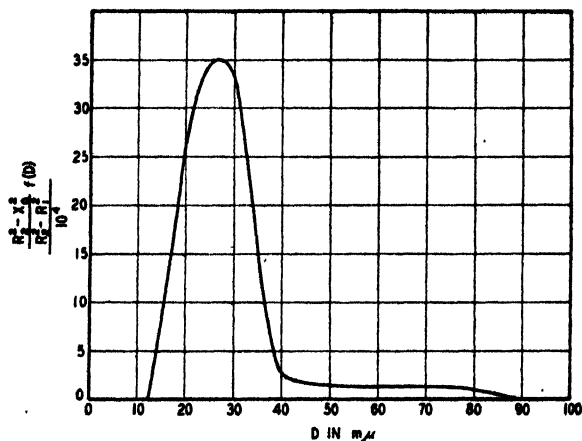


FIG. 6. Evaluation of line integral over $f(D)$ at $y = 10$ cm.
Area = W at $y = 10$ cm.

The distribution curve shows that the majority of the particles in this highly colloidal bentonite have equivalent spherical diameters, the majority of which range from 15 to 35 $m\mu$ with both larger and smaller sizes present. For comparison calculated curves are presented showing how the experimental data should have looked if the distribution function had taken one

of the other forms indicated. Corresponding curves on figures 4 and 5 are represented by the same number.

By systematically centrifuging samples similar to the one whose distribution curve is shown, as well as those heavier portions taken off by gravity settling, a series of fractions of different average particle sizes will be obtained for the gelation tests.

CONCLUSION

In connection with a new series of studies regarding the effect of particle size on thixotropy and gel structure in general, it was necessary to develop a new method for making particle-size fractionations and measuring particle-size distribution curves of systems existing in the true colloidal range of matter. The new method employing the supercentrifuge has been described and should prove useful in many lines of colloidal research, since it employs relatively inexpensive equipment compared to other methods in use at present.

Future improvements in the accuracy of this method will probably have to come in the design of a supercentrifuge especially adapted for measurements of particle size. At the present time the purpose was to develop the theory necessary to the measurement of distribution curves in truly colloidal systems with a machine standard on the market and well within the financial reach of many laboratories. It is felt that the general theory as embodied in equation 7 is satisfactory, and that curves obtained with the present machines are reasonably accurate. Future experimental work now in progress will show to what extent the simplification introduced by equation 8 is justified. Finally it must be remembered that the supercentrifuge is the best means available at the present time for making rational particle-size fractionations in systems containing the very finest colloidal particles.

REFERENCES

- (1) BRADFIELD: *J. Phys. Chem.* **32**, 208 (1928).
- (2) BRADFIELD: *J. Am. Chem. Soc.* **45**, 1243 (1923).
- (3) FREUNDLICH: *Actualités Scientifiques et Industrielles*, No. 267, The Colloidal State, I (Thixotropy). Paris (1935).
- (4) KUHN: *Kolloid-Z.* **37**, 365 (1925).
- (5) LAMB: *Hydrodynamics of Fluids*, 3rd edition, p. 543 (1906).
- (6) LENOIR, S. M.: Thesis, Department of Chemical Engineering, Massachusetts Institute of Technology, 1936.
- (7) MARSHALL: *Trans. Ceramic Soc.* **30**, 81 (1931).
- (8) MCBAIN AND O'SULLIVAN: *J. Am. Chem. Soc.* **57**, 2631-41 (1935).
- (9) MOORE, FRY, AND MIDDLETON: *Ind. Eng. Chem.* **13**, 527 (1921).
- (10) ODÉN: *Sedimentation Analysis and its Application to the Physical Chemistry of Clays and Precipitates*, in *Alexander's Colloid Chemistry*, Vol. I, p. 861. The Chemical Catalog Co., Inc., New York (1926).

- (11) PRYCE-JONES: J. Oil Colour Chem. Assoc. **17**, 305 (1934).
- (12) RUSSELL: Proc. Roy. Soc. London **154A**, 554 (1936).
- (13) SQUIRES, L., AND SQUIRES, W.: Trans. Am. Inst. Chem. Engrs., in press (1936).
- (14) STOKES: Phil. Mag. **29**, 60 (1846).
- (15) SVEDBERG AND ESTRUP: Kolloid-Z. **9**, 259 (1911).
- (16) SVEDBERG AND RINDE: J. Am. Chem. Soc. **45**, 943 (1923).
- (17) SZEGVARI AND SCHALEK: Kolloid-Z. **32**, 318; **33**, 326 (1923).
- (18) WESTGREN: Z. anorg. allgem. Chem. **94**, 193 (1916).

ADSORPTION OF IONS AND THE PHYSICAL CHARACTER OF PRECIPITATES. II

FERRIC OXIDE AND BENTONITE PRECIPITATES¹

G. E. CUNNINGHAM, H. E. GABLER, AND W. S. PEACHIN

Department of Chemistry, Clarkson College of Technology, Potsdam, New York

Received June 11, 1936

Among the various factors which influence the physical nature of a precipitate, the specific effect of adsorbed ions is often one of the most important. The importance of choosing the proper medium for the formation of precipitates in analytical work is too familiar to require discussion here.

The experiments here recorded were suggested by previous observations made by Cunningham in collaboration with Weiser (5) on sulfur precipitates formed by salting Odén's sulfur sol. Stingl and Morawski (4) and Odén (3) had recorded various salts as giving precipitates ranging macroscopically from gelatinous through flocculent, slimy, and fine-grained to plastic in character, depending upon the precipitating ion used. The work of Weiser and Cunningham showed that, in the last analysis, these precipitates were either gelatinous or non-gelatinous, depending upon the degree of hydration of the ions adsorbed. In the case of the formation of plastic sulfur, the neutralizing ions did not carry with them sufficient protective water to prevent complete coalescence of the particles. In the case of a gelatinous precipitate, the neutralizing ions not only carried sufficient water to form a protective coating about the micelles and prevent contact of sulfur to sulfur, but the protective water at the same time usually acted as an adhesive, loosely binding the precipitated particles together. Ions of intermediate hydration gave intermediate types of precipitates.

Weiser and Cunningham made motion pictures² through the ultramicroscope which showed the outflow of dense, adsorbed water into ordinary supernatant water as a slightly adsorbed, highly hydrated ion was displaced by a highly adsorbed, slightly hydrated ion added to the supernatant liquid. At the same time the sulfur micelles usually coalesced,

¹ Presented at the Thirteenth Colloid Symposium, held at St. Louis, Missouri, June 11-13, 1936.

² Presented at the Sixth Colloid Symposium, held at Toronto, Canada, June, 1928.

forming a particle of plastic sulfur very much smaller than the original clump. In an extreme case, the shrinkage was to less than 0.5 per cent of the original volume.

Some views taken from the motion pictures are reproduced from the original article (5) in figure 1.

In view of the results obtained with sulfur, it seemed reasonable to expect that precipitates of substances not exhibiting the coalescing tendency of amorphous sulfur would be more or less gelatinous, depending upon the degree of hydration of adsorbed ions. Since the bulk of the sulfur clumps varied so greatly with the amount of adsorbed water, it seemed feasible to compare various precipitates on a basis of their bulk.

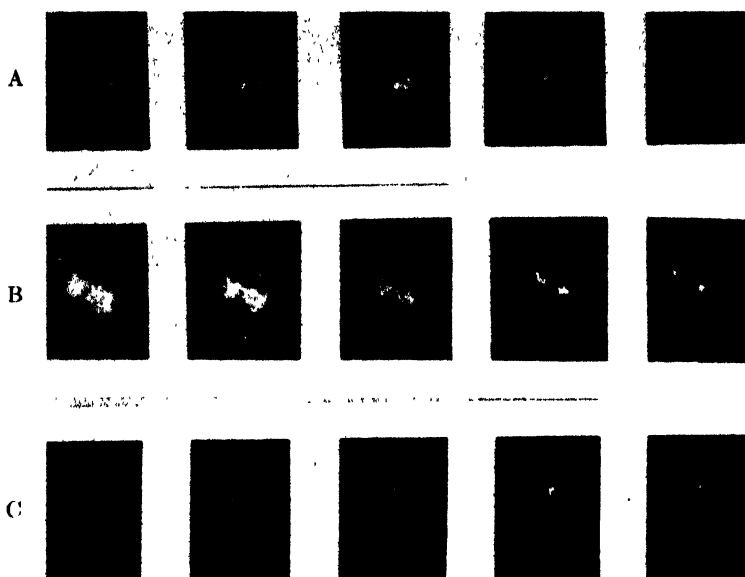


FIG. 1. Ultramicroscopic views of the shrinkage of sulfur clumps on displacing a slightly adsorbed, highly hydrated ion by a highly adsorbed, slightly hydrated ion. A, Li^+ displaced by K^+ ; B, Li^+ displaced by Cs^+ ; C, Li^+ displaced by Ba^{++} .

The effects of varying both positive and negative adsorbed ions on both a positive colloid, ferric oxide, and a negative colloid, bentonite, were studied.

EXPERIMENTAL PROCEDURE

For the purpose of forming the precipitates under uniform conditions, the Weiser mixing device (6) was used in all cases. This device consists of a smaller test tube sealed in the bottom of a larger one. One of the two liquids to be mixed is placed in each compartment, the larger tube is then stoppered, and the apparatus is shaken quickly and vigorously.

After forming the precipitates in the above manner, they, together with their supernatant liquids, were poured into $5 \times \frac{1}{2}$ in. test tubes, centrifuged for five minutes, and allowed to stand. After at least two days, the depths of the precipitates were measured with a millimeter scale. The actual

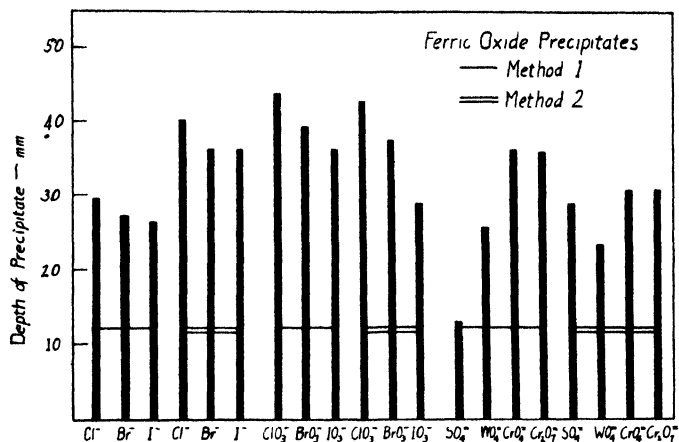


FIG. 2. Comparison of the bulks of ferric oxide precipitates obtained by varying the precipitating ion

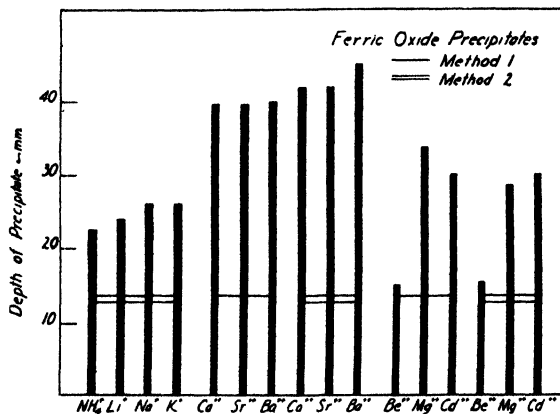


FIG. 3. Comparison of the bulks of ferric oxide precipitates obtained by varying the stabilizing ion

volumes were not recorded, but the capacity of the test tubes of the size used is about 1 cc. per 6-mm. depth. The data are recorded in the charts, figures 2 to 5.

The individual procedures are described more fully in the following paragraphs.

Ferric oxide precipitates

Method 1. Each precipitate was formed separately by placing 1 cc. of *N* ferric chloride in the inner compartment of the mixing device and 1 cc. of *N* sodium hydroxide plus 15 cc. of a normal solution of the salt supply-

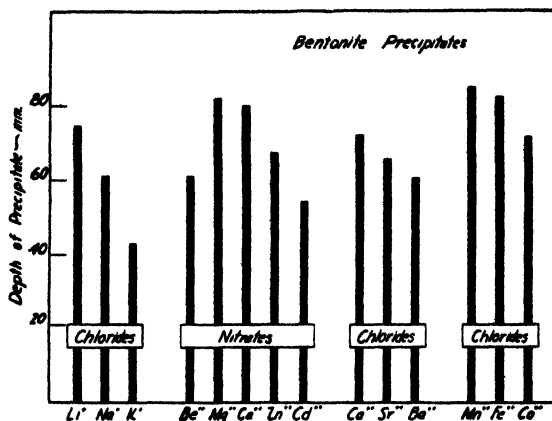


FIG. 4. Comparison of the bulks of bentonite precipitates obtained by varying the precipitating ion

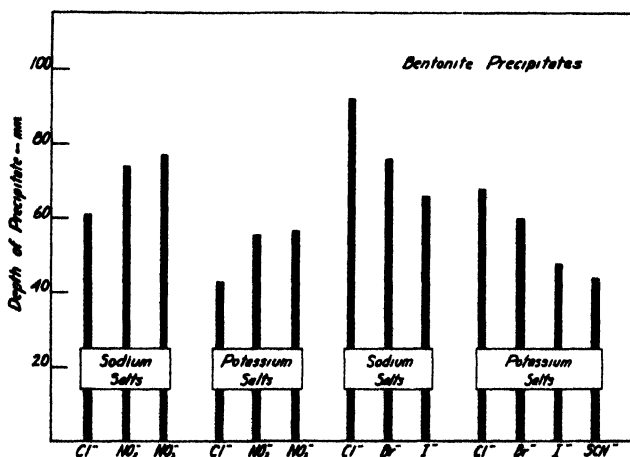


FIG. 5. Comparison of the bulks of bentonite precipitates obtained by varying the stabilizing ion

ing the ion to be studied in the outer compartment. The calculated mass of the ferric oxide was in each case 0.036 g. The results are indicated in figures 2 and 3.

Method 2. A ferric oxide sol was prepared by adding 100 cc. of *N* sodium hydroxide to 900 cc. of $\frac{2}{3}$ *N* ferric chloride, while stirring. This pro-

cedure resulted in a ferric oxide sol in 0.5 *N* ferric chloride. The sol was dialyzed for ten days, until the dialyzate, on evaporation to one-tenth its volume, showed no test for chloride.

To form the precipitates, 2-cc. portions of this sol were placed in the inner compartment of the mixer and 15-cc. portions of *N* salt solutions were placed in the outer compartment. By evaporation of 25-cc. portions of the sol, it was found that the mass of solid contained in 2 cc. of sol was 0.045 g. The results are indicated in figures 2 and 3.

All the values plotted in figures 2 and 3, for ferric oxide precipitates, were measured after the precipitates had been standing six months.

Bentonite precipitates

A bentonite sol was prepared by adding 4 parts of powdered bentonite to 100 parts of boiling water, with stirring, and allowing to stand at least two days before using. To form the precipitates, 10 cc. of sol and 10 cc. of 2 *N* salt were mixed in the mixing device. Each precipitate contained 0.4 g. of bentonite. The results are indicated in figures 4 and 5. All bentonite precipitates stood at least two days before being measured.

DISCUSSION OF RESULTS

There is no good agreement among various workers or methods as to the actual degree of hydration of ions. In fact, there is some disagreement as to their order of hydration. Recent investigators (1, 2) have claimed that the degree of hydration is a linear function of the electrostatic charge on the ion. In general, the degree of hydration decreases as the atomic weight increases, for the ions of elements in a given family in the periodic classification.

As far as possible, the ions in the charts (figures 2 to 5) have been grouped according to the periodic classification. Runs plotted on vertical depth-lines tied together by horizontal tie-lines were made simultaneously. Results not tied together by horizontal lines in the charts are not to be compared with one another for the reason that, since they were made at different times, the sols were in different stages of ageing.

With ferric oxide, the bulks of the precipitates obtained with halogen-containing ions by the first method (metathetical formation of ferric oxide in the presence of various salts) were in the order $\text{Cl}^- > \text{Br}^- > \text{I}^-$ and $\text{ClO}_3^- > \text{BrO}_3^- > \text{IO}_3^-$. By the second method (salting out the dialyzed sol), the order was $\text{Cl}^- > \text{Br}^-$, I^- , and $\text{ClO}_3^- > \text{BrO}_3^- > \text{IO}_3^-$. In each case the order is as predicted.

The bulks of the ferric oxide precipitates obtained by the first method with the divalent ions studied were in the order $\text{CrO}_4^{--} > \text{Cr}_2\text{O}_7^{--} > \text{WO}_4^{--} > \text{SO}_4^{--}$. By the second method, the order was $\text{CrO}_4^{--} > \text{Cr}_2\text{O}_7^{--} > \text{SO}_4^{--} > \text{WO}_4^{--}$, the order of SO_4^{--} and WO_4^{--} being reversed. No information

was available to the authors as to the findings of other workers with regard to the hydration of these ions.

The bulks of the ferric oxide precipitates obtained with various cations by the first method were in the order $\text{Ba}^{++} > \text{Sr}^{++}$, Ca^{++} and $\text{Mg}^{++} > \text{Cd}^{++} > \text{Be}^{++}$. By the second method, the order was: K^+ , $\text{Na}^+ > \text{Li}^+ > \text{NH}_4^+$; $\text{Ba}^{++} > \text{Sr}^{++}$, Ca^{++} ; $\text{Cd}^{++} > \text{Mg}^{++} > \text{Be}^{++}$. With the exception of the case $\text{Mg}^{++} > \text{Cd}^{++}$ by the first method, the positions of the ions in these series are all the reverse of those expected on a basis of their positions in the periodic classification. However, since ferric oxide is a positive sol, these are stabilizing ions, and the heavier ions are much more highly adsorbed than the lighter ones. It is believed that the heavier stabilizing ions are so highly adsorbed as to bring about the adsorption of a sufficiently larger quantity of negative precipitating ions to account for the increased bulk of the precipitate. No attempt has been made to prove this hypothesis but, in the absence of evidence to the contrary, it seems reasonable.

With bentonite, a negative sol, the bulks of the precipitates obtained with various cations were in the order: $\text{Li}^+ > \text{Na}^+ > \text{K}^+$; $\text{Mg}^{++} > \text{Ca}^{++} > \text{Zn}^{++} > \text{Be}^{++} > \text{Cd}^{++}$; $\text{Ca}^{++} > \text{Sr}^{++} > \text{Ba}^{++}$; and $\text{Mn}^{++} > \text{Fe}^{++} > \text{Co}^{++}$. With the exception of Be^{++} , these ions all fall in the order predicted.

The bentonite precipitates obtained in the presence of various stabilizing ions ran in the order $\text{NO}_3^- > \text{NO}_2^- > \text{Cl}^-$ and $\text{Cl}^- > \text{Br}^- > \text{I}^- > \text{SCN}^-$. As far as predictable from the periodic classification, the positions of these ions are in agreement with the theory.

In practically all the above cases, the order of the ions is in agreement with the familiar Hofmeister series for their effect on the swelling of gelatin. That is, those ions which, in these experiments, gave precipitates of least bulk are the ones which make gelatin the least gelatinous, or most fluid, and *vice versa*. The indication is that in the case of the thinner gelatin gel there is less bound water and more lubricating water than in the thicker gel.

The results of these experiments could not be duplicated with arsenious sulfide sol, for the reason that the arsenious sulfide itself is not gelatinous enough to give precipitates of sufficient bulk to show the differences in bulk. This does not mean that the adsorbed ions have no effect on the character of the micelles, however.

It is hoped that the results of these experiments may be found of practical use in the control of the nature of precipitates and the consistency of pastes.

SUMMARY

1. A study has been made of the effect of adsorbed ions on the bulks of ferric oxide and bentonite precipitates.

2. The bulk of the precipitate is symbatic with the degree of hydration of the adsorbed ions.

REFERENCES

- (1) BRINTZINGER AND RATANARAT: *Z. anorg. allgem. Chem.* **222**, 113 (1935).
- (2) BRINTZINGER, RATANARAT, AND OSSWALD: *Z. anorg. allgem. Chem.* **223**, 101 (1935).
- (3) ODÉN: *Der kolloide Schwefel*, pp. 134, 157. Akademische Buchhandlung, Upsala (1912).
- (4) STINGL AND MORAWSKI: *J. prakt. Chem.* [2] **20**, 76 (1879).
- (5) WEISER AND CUNNINGHAM: *Colloid Symposium Monograph* **6**, 319-41 (1928); *J. Phys. Chem.* **33**, 301-16 (1929).
- (6) WEISER AND MIDDLETON: *J. Phys. Chem.* **24**, 48 (1920).

COACERVATION OF AMYLOPHOSPHORIC ACID AND PROTEINS¹

P. KOETS

van't Hoff Laboratory, University of Utrecht, Utrecht, Holland

Received June 11, 1936

When hydrophilic colloids of opposite electric charge are mixed in solution, separation of a complex may be observed over a range of concentration of the components. In most cases this complex is of a liquid nature, separating out in the form of microscopic droplets. After some time these drops may unite to form a viscous liquid layer at the bottom of the container. This phenomenon has been observed before, but its underlying principles have been recognized lately by Bungenberg de Jong and Kruyt (3, 1), who have given the name "coacervation" to this separation of a liquid phase from solutions of hydrophilic colloids ("complex coacervation" when two or more colloid components are involved). They assume that the difference in sign of the charge causes the micelles to approach, their double layers partly discharging each other. Owing to this approach the outer and less firmly bound water of hydration will be removed, but ultimately the approach will come to a halt, when the force of attraction, due to the contrast in charge, will be balanced by the resistance of the more rigidly bound water of hydration. They therefore consider the resulting droplet to be a conglomerate of positive and negative micelles which remain individually next to each other, each retaining part of its water of hydration (*acervus* = swarm, heap). They showed that this phenomenon occurs generally in solutions of hydrophilic colloids, even when only one colloid is involved, the opposition in charge being located in this case on one and the same surface (either naturally as in the proteins or brought about artificially by adsorption of polyvalent ions of a charge opposite to that of the colloid).

From measurements of viscosity it could be shown that partial dehydration takes place, the viscosity of the mixtures of the two colloid solutions being considerably lower than that calculated from additivity. On the other hand, these authors showed that every influence which diminishes the electric charge of the micelles and therefore lowers the attraction of the colloid particles, prevents the formation of the coacervate

¹ Presented at the Thirteenth Colloid Symposium, held at St. Louis, Missouri, June 11-13, 1936.

or disperses the complex again after it has formed. As two opposite potentials are involved, this influence is found for both cations and anions, the concentrations required being lower the higher the valency of the ion (double Schulze-Hardy rule).

These coacervates may separate out in any form ranging from a fairly liquid fluid to a more or less plastic mass. The better the opposite charges are balanced, the higher the contrast in charge, and the greater will be the mutual dehydration. On the other hand, the effect of the attraction can be increased by the addition of dehydrating agents. It was found by these authors that the tendency of a hydrophilic colloid to enter into coacervation depends on its density of charge. Nucleic acid, having a high density of charge, combines readily with other biocolloids, and the resultant coacervate is highly resistant to electrolytes. No coacervates could, however, be obtained with the carbohydrate amylose as a component, a fact which may perhaps be significant in connection with the position of amylose as a reserve substance in nature.

The negative electric charge of amylose is probably due, at least in part, to the dissociation of the hydroxyl groups in the surface of the micelle. This dissociation is a function of the hydrogen-ion concentration of the solution. The charge is small in comparison to that of other hydrophilic colloids as agar or gum arabic, where more strongly dissociated groups resulting from sulfuric acid esters or from the carboxyl group contribute to it. In alkaline medium the dissociation of the hydroxyl groups of amylose is favored and, eventually, a completely developed double layer can be built up. In neutral or slightly acid solution, however, the negative charge of amylose is too small to bring about coacervation with positive proteins, the mutual attraction being too small to overcome the repelling force of the micelle hydration.

The character of amylose can now be changed completely by introducing strongly negative groups into the surface of the micelle, for instance, by esterification with phosphoric acid. The resulting amylophosphoric acid shows an appreciable anodic migration and possesses a sufficiently high density of charge to be able to combine with positively charged proteins to droplets and floccula, which in their general behavior show the character of coacervates.

We prepared amylophosphoric acid following the method described by Kerb (7, 21). Six grams of "amylum soluble Merck," free from nitrogen, were dissolved in the usual way in 150 cc. of hot water. After cooling, the vessel was placed in ice and 24 g. of pure calcium carbonate was stirred in. In the course of two hours a solution of 5 g. of phosphorus oxychloride in 10 cc. of chloroform was gradually added under continuous vigorous stirring. An equal amount of water was then added and the precipitate centrifuged off after it had settled overnight. From the clear solution

calcium amylophosphate was precipitated by addition of an equal volume of alcohol; the precipitate was washed with 50 per cent alcohol and redissolved in water. The solution was then electrodyalyzed until free from calcium. In the mean the amylophosphoric acid so prepared contained 0.5 per cent of phosphorus pentoxide, calculated on the dry substance.

When solutions of amylophosphoric acid and of a protein are mixed in different proportions at a pH below the isoelectric point of the protein, a pronounced turbidity, caused by the formation of microscopic droplets, may be observed in a distinct region of proportions of the two colloids. Gradually, the liquid droplets change to solid floccula and settle to the bottom of the vessel. Addition of alkali in small quantities causes the turbidity to disappear as the charge on the protein is reduced and ultimately reversed. Addition of acid has the same effect, as the charge of both colloids is diminished.

In order to establish further the coacervate nature of the new phase, we measured the viscosities of the mixtures in comparison to those of the two components. When two solutions of hydrophilic colloids are mixed and no interaction of the micelles takes place, the viscosities of the mixtures can be calculated from those of the two components by the rule of additivity. In the case of oppositely charged colloids a deviation from additivity is observed, which is greater the more completely the opposite charges balance each other (2, 4).

AMYLOPHOSPHORIC ACID-GELATIN

We used a 0.12 per cent solution of amylophosphoric acid and a 0.12 per cent solution of a pure gelatin (isoelectric point, $\text{pH} = 5.0$). The viscosities were measured in an Ostwald viscometer at 40°C . The required pH values of the solutions were obtained by adding the necessary amounts of sodium hydroxide or hydrochloric acid, and were controlled by means of a quinhydrone electrode and by color indicators. The results are collected in table 1 and represented in figure 1. The fourth column of the table gives the relative viscosities as found experimentally; the fifth, those calculated for additivity of the viscosities of the two unmixed solutions and their proportion in the mixture.

The results are in complete accord with what may be expected in the case of a coacervate. The lower the pH, that is the farther the gelatin is removed from its isoelectric point (and therefore the larger its positive charge), the less is the total amount of gelatin necessary to bring about the minimum in the additivity curve. The optimum of attraction of the opposite charges of the micelles is found at a pH of approximately 3.5.

Separation of coacervate droplets is found not only at the colloid proportions denoted by the minima, but also at some distance on either side of the minima. The droplets which separate at the conditions of the

minimum are electrically neutral, and they show practically no cataphoretic movement. On either side of the minimum, however, the droplets show an outward electrophoretic charge of the sign of the colloid which predominates in the complex. At the proportion of exact balance, the

TABLE 1
Viscosities of mixtures of amylophosphoric acid and gelatin sols

pH	AMYLO- PHOSPHORIC ACID SOL	GELATIN SOL	$\left(\frac{\eta_s - \eta_0}{\eta_0}\right)_{\text{exptl.}}$	$\left(\frac{\eta_s - \eta_0}{\eta_0}\right)_{\text{calcd}}$	PER CENT OF ADDITIVITY
	cc	cc.			
2.6	100		0.075		100
	95	5	0.023	0.082	28.1
	80	20	0.027	0.102	26.5
	50	50	0.079	0.143	55.4
	20	80	0.165	0.184	89.7
		100	0.211		100
3.5	100		0.109		100
	95	5	0.022	0.113	19.5
	80	20	0.019	0.126	15.1
	50	50	0.052	0.151	34.4
	20	80	0.118	0.176	67.0
		100	0.193		100
4.2	100		0.111		100
	90	10	0.064	0.108	59.3
	80	20	0.041	0.105	39.0
	50	50	0.023	0.094	24.4
	20	80	0.043	0.085	50.6
		100	0.078		100
4.6	100		0.113		100
	80	20	0.064	0.104	61.5
	50	50	0.028	0.090	31.2
	30	70	0.028	0.081	34.6
	20	80	0.035	0.076	46.1
		100	0.067		100
4.9	100		0.115		100
	80	20	0.099	0.105	94.3
	50	50	0.066	0.090	73.3
	30	70	0.059	0.080	73.7
	20	80	0.061	0.075	81.3
		100	0.065		100

micelles can approach each other to a maximum extent and the hydration is therefore at a minimum. When there is a preponderance of either of the two charges in the complex, the mutual repulsion of these excess charges causes the system to be less condensed and more hydrated.

AMYLOPHOSPHORIC ACID-LEUCOSIN

The viscosities of mixtures of a sol of amylophosphoric acid and of one of leucosin, prepared from wheat, were determined at 30°C. The results are tabulated in table 2 (figure 2). The phenomena are similar in all respects to those described for the system amylophosphoric acid-gelatin.

AMYLOPHOSPHORIC ACID-POTATO ALBUMIN

An albumin from potato was obtained by saturating the juice, squeezed out by means of a hydraulic press, with ammonium sulfate. The precipitated impure proteins were shaken with cold water, and the filtered solution again saturated with ammonium sulfate. This was repeated four

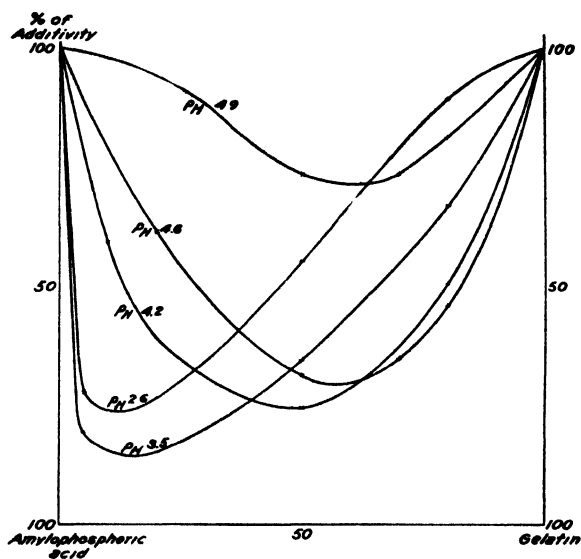


FIG. 1

times. The original deep-green color of the juice had then largely disappeared. The solution of the last precipitate in water was submitted to electrodialysis. Some globulin which separated out during this last process was removed by filtration. The viscosities of the sol mixtures were measured at 30°C. The results are represented in table 3 (figure 3).

The following general characteristics which these coacervates have in common may be mentioned. Immediately after mixing of the solutions, when the coacervate still exists in the form of liquid drops, it can be dissolved again completely by addition of either alkali, or acid, or neutral electrolytes. In the case of peptization with neutral salts in small quantities, the coacervate can be made to reappear by addition of alcohol or

TABLE 2

Viscosities of mixtures of amylophosphoric acid and leucosin sols

pH	AMYLO- PHOSPHORIC ACID SOL	LEUCOSIN SOL	$\left(\frac{\eta_s - \eta_0}{\eta_0}\right)_{\text{exptl.}}$	$\left(\frac{\eta_s - \eta_0}{\eta_0}\right)_{\text{calcd.}}$	PER CENT OF ADDITIVITY
2.7	cc.	cc.			
	100		0.111		100
	95	5	0.049	0.107	45.8
	80	20	0.035	0.096	36.4
	50	50	0.039	0.073	53.5
3.0		100	0.035		100
	100		0.111		100
	95	5	0.065	0.107	60.7
	80	20	0.030	0.096	31.3
	50	50	0.032	0.072	44.5
4.0	20	80	0.037	0.049	75.5
		100	0.033		100
	100		0.112		100
	80	20	0.049	0.095	51.6
	50	50	0.034	0.070	48.5
4.5	20	80	0.033	0.044	74.9
		100	0.027		100
	100		0.114		100
	80	20	0.076	0.095	80.1
	50	50	0.044	0.067	65.7
	20	80	0.027	0.038	76.1
		100	0.020		100

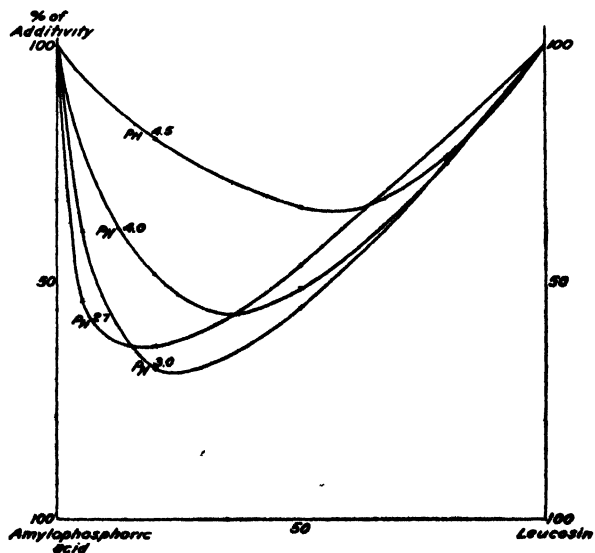


FIG. 2

TABLE 3

Viscosities of mixtures of amylophosphoric acid and albumin sols

pH	AMYLO- PHOSPHORIC ACID SOL	ALBUMIN SOL	$\left(\frac{\eta_s - \eta_0}{\eta_0}\right)_{\text{exptl}}$	$\left(\frac{\eta_s - \eta_0}{\eta_0}\right)_{\text{calcd}}$	PER CENT OF ADDITIVITY
	cc	cc			
2.6	100		0.115		100
	90	10	0.071	0.107	66.3
	80	20	0.055	0.098	56.1
	50	50	0.040	0.072	55.5
	25	75	0.034	0.050	68.0
		100	0.028		100
3.5	100		0.120		100
	95	5	0.085	0.115	73.9
	75	25	0.037	0.096	38.6
	50	50	0.023	0.073	31.5
	25	75	0.021	0.049	42.8
		100	0.025		100
4.4	100		0.122		100
	80	20	0.069	0.101	68.4
	50	50	0.031	0.070	44.3
	25	75	0.024	0.044	54.5
		100	0.018		100

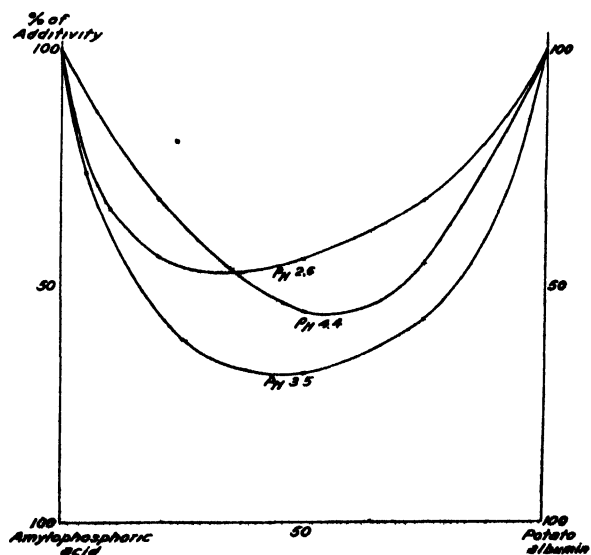


FIG. 3

another dehydrating agent. The droplets of these coacervates have, however, a pronounced tendency to change to floccula on standing. They then become, at the same time, more resistant to dispersion; peptization may sometimes be obtained by potassium thiocyanate or alkali.

AMYLOPECTIN

The observation that amylose can enter into coacervation with proteins only after its density of charge has been increased, for instance, by esterification with phosphoric acid, leads to some new speculations on the nature of amylopectin. It is to the presence of amylopectin that the high viscosity and the paste-forming qualities of a starch solution are ascribed. A solution of native starch in water is, however, not a true colloidal solution. Its viscosity does not follow Poiseuille's law, indicating the presence of micelle conglomerates or gel fragments in the solution (12, 6). In the ultracentrifuge the amylopectin settles quickly and long before the amylose (8); even in the ordinary centrifuge, the amylopectin fraction can be separated from the bulk of the solution (22).

We may consider a solution of native starch to be a solution of amylose in which amylopectin, in the form of gel fragments, is more or less finely suspended.

Samec (18, 14, 20, 17) showed that amylophosphoric acid is a component of the amylopectin and that, apart from silicic acid and fatty acids, it contains nitrogenous substances often to a considerable extent. In potato starch the nitrogen content is small compared to that of phosphoric acid; from wheat, amylopectin fractions can be obtained in which the nitrogen content is equal to or even greater than the content of phosphoric acid. Samec assumed that protein and amylophosphoric acid are bound "salt-like" in amylopectin, but later he himself showed this view to be unsatisfactory (16).

We suggest that it may be of advantage to consider amylopectin to be of the nature of a coacervate as described in the first part of this paper, that is to say, that the binding of the components is not one of classical chemical mass stoichiometry, but rather a balancing of the opposite charges of the colloid micelles involved, these micelles largely retaining their individuality in the complex.

It has been shown that the ultimate electrophoretic charge of the coacervate drops will depend on the proportions of two colloids present. In potato starch the negative component largely predominates over the positive protein. In accordance with the above theory one would expect the resulting coacervate to have a negative charge and to move cataphoretically to the anode, as is found experimentally. Similarly Samec and Antonovic (19) found fractions of wheat amylopectin which differed in their cataphoretic behavior, those in which phosphoric acid is in excess moving to the

anode, and those in which protein is in excess actually moving or at least having a tendency to move to the cathode. Samec's original assumption that the high viscosity of starch solutions is solely due to the phosphoric acid content of the amylopectin has been the subject of controversy (13, 23, 6, 5). Indeed the viscosity of a solution of amylophosphoric acid, obtained from pure amylose, is not very much higher than that of a solution of amylose. The excessively high viscosities originally mentioned by Samec may be explained by the fact that the amylose which he esterified with phosphoric acid was obtained from amylopectin fractions from which the phosphoric acid had been removed previously by saponification. The nitrogenous substances probably remained in solution and were able to give rise to new coacervates as soon as amylophosphoric acid was formed again. These complexes, remaining dispersed in solution as gel fragments, could then cause a high viscosity. Indeed we found that the complexes of amylophosphoric acid and proteins described in this paper can be dispersed by boiling in a solution of pure amylose, from which they do not separate again on cooling. The viscosity of a solution so obtained shows an appreciable increase compared to that of an equally concentrated amylose solution.

Samec distinguished amylopectin fractions according to the color produced with an iodine-potassium iodide solution, the color changing from blue to red the higher the nitrogen content of the fraction. Whereas a solution of amylophosphoric acid gives a blue color with this reagent, we found that the color obtained with the coacervates previously described turned from blue to violet and red, the more the protein content was increased.

Many experiments have been recorded in which the properties of native starch have been changed by treatment with either dilute hydrochloric acid or potassium hydroxide. From our point of view, removal of protein from wheat amylopectin in larger proportion than phosphoric acid (15) must necessarily lead to a product resembling potato amylopectin (the coacervate, by removal of the positive component, changing to a complex in which the negative amylophosphoric acid micelles predominate), and ultimately to a product having the properties of a soluble starch (the system being incapable of coacervation owing to the absence of one of the components).

Considering potato amylopectin to be a coacervate complex with a large negative surplus charge, one may expect it to be able to undergo renewed coacervation with positively charged protein, ultimately leading to a product resembling wheat amylopectin, as has indeed been found (16, 11). Many authors have described amylopectin as differing only from amylose by being more interlocked (more dense) and less hydrated (24, 9, 10, 5). These properties are inherent in coacervate complexes, the opposite charges

causing the micelles to approach more closely to each other and to be less hydrated than in free colloidal solution.

In conclusion the author wishes to express his thanks to Prof. H. R. Kruyt, in whose laboratory this investigation was carried out, for his continual interest.

REFERENCES

- (1) BUNGENBERG DE JONG AND COLLABORATORS: *Biochem. Z.* 1929-32. For summary see BUNGENBERG DE JONG: *Protoplasma* **15**, 110 (1932).
- (2) BUNGENBERG DE JONG AND DEKKER: *Biochem. Z.* **212**, 318 (1929).
- (3) BUNGENBERG DE JONG AND KRUYT: *Proc. Roy. Acad. Amsterdam* **32**, 849 (1929); *Kolloid-Z.* **50**, 39 (1930).
- (4) BUNGENBERG DE JONG AND ONG SIAN GWAN: *Biochem. Z.* **221**, 166 (1930).
- (5) HIRST, PLANT, AND WILKINSON: *J. Chem. Soc.* **1932**, 2375.
- (6) KARRER AND KRAUSZ: *Helv. Chim. Acta* **12**, 1144 (1929).
- (7) KERR: *Biochem. Z.* **100**, 3 (1919).
- (8) LAMM: *Kolloid-Z.* **69**, 44 (1934).
- (9) LEPIŠCHKIN: *Kolloid-Z.* **32**, 42 (1923).
- (10) NOWOPOKROWSKI: *Kolloid-Z.* **52**, 302 (1930).
- (11) VON PRZYLECKI AND DOBROWOLSKA: *Biochem. Z.* **245**, 388 (1932); **248**, 16 (1932).
- (12) ROTHLIN: *Biochem. Z.* **98**, 34 (1919).
- (13) SAMEC: *Kolloidchemie der Stärke*, pp. 26, 27.
- (14) SAMEC: *Biochem. Z.* **186**, 337 (1927); **195**, 72 (1928).
- (15) SAMEC: *Kolloidchem. Beihefte* **33**, 95 (1931).
- (16) SAMEC: *Kolloidchem. Beihefte* **40**, 449 (1934).
- (17) SAMEC: *Z. ges. Getreide-Mühlenw. Backereiwesen* **21**, 111 (1934).
- (18) SAMEC: *Trans. Faraday Soc.* **31**, 395 (1935).
- (19) SAMEC AND ANTONOVIC: *Kolloidchem. Beihefte* **23**, 377 (1926).
- (20) SAMEC AND BLINC: *Kolloidchem. Beihefte* **30**, 163 (1930).
- (21) SAMEC AND MAYER: *Kolloidchem. Beihefte* **16**, 91 (1929).
- (22) SHERMAN AND BAKER: *J. Am. Chem. Soc.* **38**, 1885 (1916).
- (23) TAYLOR AND WALTON: *J. Am. Chem. Soc.* **51**, 3431 (1929).
- (24) DE VRIES: *Botan. Jahresber.* **1**, 122 (1885).

KELVIN SINGLE-POTENTIAL DIFFERENCES

WILDER D. BANCROFT AND JERMAIN D. PORTER

Department of Chemistry, Cornell University, Ithaca, New York

Received October 15, 1936

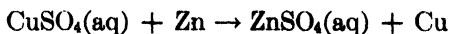
In 1802 Volta (18) expressed the belief that most of the electromotive force of a voltaic cell was generated at the junction of the two metals which dipped into the solution or solutions. This could not be the whole truth, because cases are known in which we can reverse the flow of current through the cell, and because it is possible to make a cell having quite an electromotive force out of one metal and two suitably chosen solutions. Volta's theory was known as the contact theory and has been held from that day to this by most physicists, with Lodge as the outstanding exception.

The chemists felt that the chemical reaction furnished the electrical energy and that consequently most of the potential difference was set up where the chemical change took place,—at the metal-liquid and liquid-liquid interfaces. Some potential difference must be set up at the metal-metal interface because of the behavior of thermocouples. Since the thermoelectric force is very small, the chemists hoped that the contact potentials between metals were also very small,—which does not follow at all. A few chemists, Ostwald among them, claimed that the Peltier effect was a measure of the potential difference between two metals, but this deduction did not last long. If the argument had been valid (9), people would have devised some method of determining the potential difference between metal and solution from the Peltier effects for the metal-solution junctions. The so-called chemical theory of the voltaic cell has been held by most chemists, Sir Humphry Davy and Langmuir being two conspicuous exceptions.

When it was shown by Helmholtz that there was a definite relation between the electromotive force of a reversible cell, the heat of reaction, and the temperature coefficient of the electromotive force, it seemed to most chemists that the century-old contest was over, because there was nothing left for the metal-metal contact except values so small that they were lost in the errors of determination of the three important terms (4). It does not seem to have struck any chemist as curious that Helmholtz (13) should continue to believe in the contact theory and should develop it in his Faraday Lecture. Since there is no transport of ponderable matter

in metallic conduction, it is a mistake to talk about the heat of formation of brass in connection with the Daniell cell, as Lodge does (17).

If the heat-equivalent of the contact potential is contained in the heat of reaction as determined by the chemist, there is no difficulty and the metal-metal potential may have any value in reason. This was seen clearly by Gurney (11). "A chemical change such as



carried out as a test-tube reaction, does not appear to be connected with any electrical Volta potential difference; hence the parallelism between the chemical series and the Volta series appears to be merely fortuitous, or else spurious. The only method of reconciling the contending views would be to prove that by some concealed relation the heat evolved in the test-tube reaction is itself determined by the Volta potential difference characteristic of the reacting metals. If the proof of this unsuspected relation could be obtained, then certainly the controversial deadlock would disappear."

Gurney's conclusion is right, but his premises are wrong. In 1906 one of us (1) said that "the most striking characteristic of an electrolytic reaction is that it occurs in two places,—at the anode and at the cathode. This peculiarity can be made less marked by bringing the electrodes nearer and nearer together. When the distance between them vanishes we have a chemical reaction in the ordinary sense of the word and not an electrochemical reaction. Any chemical reaction therefore, which can be made to take place electrolytically, must consist (22) of an anode and a cathode process." Consequently the same amount of heat will be generated regardless of whether one carries out the reaction in the test-tube or in a voltaic cell; and consequently the heat equivalent of whatever metal-metal potential there may be will occur in both cases.

What Gurney was really trying to say was that most chemists do not realize clearly that the heat-equivalent of any metal-metal potential appears in the heat of reaction as determined by the chemist. Helmholtz would never have accepted Gurney's statement that "it is not the chemical energy which determines the value of the electromotive force."

As far back as 1847 Helmholtz (12) explained the contact potential between zinc and copper on the assumption that zinc has a higher attracting force to positive electricity. So far as we know (4), Langmuir (16) was the first physical chemist to go over to the camp of the Voltaists and, nearly seventy years after Helmholtz, he wrote that "the Volta series of the elements is determined by the magnitude of ϕ , the electron affinity." Langmuir pointed out also that recent work in physics on electron emission from heated metals, thermal effects accompanying the electron emission, photoelectric effects from metals, measurements of contact potentials, ionizing

potentials of metal vapors, single-line spectra of metal vapors "affords conclusive proof that contact potentials exist independently of chemical reactions and are of the same order of magnitude as those observed by Volta."

In the laboratories (14, 6) of Kelvin and of J. J. Thomson experiments have been performed to show that an ionized-air gap tends to eliminate the potential difference between the phases adjoining it. These experiments seem of the utmost importance. If an ionized-air gap eliminates the potential difference completely, it becomes a simple matter to take any cell and to put in an ionized-air gap at one junction after another and thereby determine all the single-potential differences. If the elimination is not complete, there will be an error in each determination of a single-potential difference, but we shall be nearer the true value than ever before. It will be a simple matter to apply the method to reversible electrodes, and the physicists (8) of the Kelvin school have always fought shy of measuring reversible electrodes.

METHOD OF MEASUREMENT

To measure the electromotive force of a cell containing metallic or solution electrodes separated by an ionized-gas gap, the conducting phases on the two sides of the ionized-gas gap must present a large enough area to each other so that sufficient ion-current can flow to equalize their potentials in a reasonable time. The grounded electrode must surround almost completely the one which is connected with the electrometer; otherwise the potential of the latter is changed more rapidly by induction from external objects than it can be equalized by the ion current.

Following Greinacher (10) and others, a compensation method was used. A potentiometer furnished the compensating potential difference, and the null instrument was a modified form of the Dolezalek electrometer, loaned us by Professor Richtmyer. It was used at a sensitivity of about 150 mm. per volt, thus enabling electromotive forces to be read to 0.01 volt. Most of the electrodes studied were difficult to reproduce to better than 0.05 volt. It is believed that the results as given are probably right to ± 0.1 volt.

In the mounting finally developed for the electrodes, the lead from the electrometer is shielded by a brass tube filled with paraffin until it approaches the paraffin base of the electrodes. It then passes into a glass tube bent in a U-shape and ends in a mercury well at the bottom of the U. The glass tube, coated with paraffin to diminish leakage of charge over its surface, passes under the grounded outer electrode, touching neither the electrode nor the table top. Its extreme end is bent horizontal to keep out occasional drippings when the electrode is covered with a solution. A platinum or copper wire attached to the bottom of the inner electrode is

bent into such a shape that it can be inserted into the mercury well in order to make connection with the electrometer. The inner electrode rests on two paraffin pillars and is held upright by the wire running into the mercury well. To minimize leakage over the surface of the insulation, the path over the paraffin is made as long as practicable.

The air gap was ionized by means of radium furnished to us by Professor Papish. When in use the radium was enclosed in a lead block having a narrow slit which permitted radiation between, and parallel to, the electrodes.

The preparation of the various electrodes is described later. Solutions were applied to the electrodes simply by flowing them over the surface, the electrodes being removed from their supports and held horizontal. It was found possible to dispense with the agar which was used in earlier experiments.

The ordinary voltaic cells, which were measured for comparison with the ionized-air cells, were set up in beakers or in calomel half-cell vessels. The electromotive forces were measured with the potentiometer and a galvanometer, no special pains being taken to get the third decimal place, since they were to be compared with the electromotive forces of the much less reproducible ionized-gas cells.

SILVER CHLORIDE CONCENTRATION CELLS

Ordinary voltaic cells without ionized-air gaps were measured first. The electrodes were platinum foil, plated with silver from a cyanide bath. They must be washed free from cyanide or they will give erratic and worthless results. One of the electrodes chloridized by anodic treatment in concentrated hydrochloric acid gave nearly the same potential (within about 5 mv.) in dilute hydrochloric acid saturated with silver chloride as an unchloridized electrode in the same solution. Hence in all of the following cells hydrochloric acid saturated with silver chloride was relied upon to form a chloride film upon the silver electrode.

The hydrochloric acid solutions were of the following concentration:

$$\begin{aligned}c_1\text{HCl} &= 0.00976\ N \\c_2\text{HCl} &= 0.484\ N\end{aligned}$$

They were saturated with silver chloride by adding freshly precipitated silver chloride and stirring mechanically for several hours. The solutions were stored in carefully cleaned bottles provided with siphons so that grease-free solution could be drawn off. This precaution seems to be important when the solutions are used in ionized-air cells.

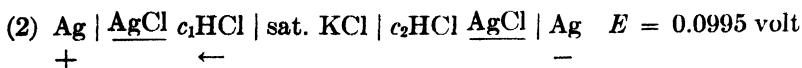
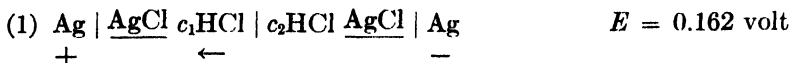
The electrodes for the ionized-air cells were made of platinum foil and were plated with silver from a cyanide bath. After a preliminary rinsing, they were washed exhaustively by boiling in repeated changes of distilled

water. The electrodes acquired a grease film particularly readily, but this could be removed by boiling in alcohol.

In making the measurements, as many cross-checks as possible were obtained. For example, both the inner and the outer electrodes were moistened with the dilute hydrochloric acid (c_1), inserted in the supports, and the electromotive force measured. It was about 0.01 volt. Then the solution on the inner electrode was replaced by $c_2\text{HCl}$. After making a measurement, both solutions (which tended to drain off and to evaporate) were renewed and the measurement repeated. If the values did not agree within 0.02–0.03 volt, the solutions were renewed again. Then $c_2\text{HCl}$ was flowed over both electrodes and the electromotive force was found to be within 0.01 volt of zero. The solution on the inner electrode was replaced with $c_1\text{HCl}$; the electromotive force was very nearly the same as it was when the outer electrode was wetted with $c_1\text{HCl}$ and the inner electrode with $c_2\text{HCl}$. This shows that the geometric asymmetry of the cell does not affect the results. Numerous checks of this sort were made. The electromotive forces were satisfactorily reproducible on the whole, provided the electrodes were washed thoroughly after plating and were free from grease.

After the electrodes have been in use for an hour or two, they no longer hold a coherent film of liquid and the results become more erratic. Occasionally, even before this happens, the electromotive force will fall for no apparent reason as much as 0.04 volt below what preceding measurements led one to expect. The great majority of the values, however, agree within ± 0.02 volt, and the cross-checks are so consistent that we believe we may disregard the few erratic ones.

As stated before, $c_1\text{HCl} = 0.00976 N$ hydrochloric acid saturated with silver chloride and $c_2\text{HCl} = 0.484 N$ hydrochloric acid saturated with silver chloride. We use the symbol $|||$ throughout this paper to denote an ionized-gas gap. All silver chloride electrodes were formed by dipping a silver electrode into one of these hydrochloric acid–silver chloride solutions. In the three cells where the silver chloride electrode is dry, the film was prepared by dipping the silver electrode into one of the solutions and allowing it to dry. The electromotive force is given the sign of the left-hand electrode, and the positive current flows from right to left through the cell when the electromotive force is positive. This is the international custom and not the one still maintained by G. N. Lewis. The arrow denotes the direction of flow of current. A summary of the data is given.



- (3) $\text{Ag} \mid \underline{\text{AgCl}} \mid c_1\text{HCl} \parallel c_2\text{HCl} \mid \underline{\text{AgCl}} \mid \text{Ag}$ $E = 0.07 \text{ to } 0.09 \text{ volt}$
 $\quad \quad \quad + \quad \quad \quad \leftarrow \quad \quad \quad -$
- (4) $\text{Ag} \mid \underline{\text{AgCl}} \parallel c_1\text{HCl} \mid \underline{\text{AgCl}} \mid \text{Ag}$ $E = -0.20 \text{ to } -0.22$
 $\quad \quad \quad - \quad \quad \quad \rightarrow \quad \quad \quad +$
 $\quad \quad \quad \quad \quad \quad \text{volt}$
- (5) $\text{Ag} \mid \underline{\text{AgCl}} \parallel c_2\text{HCl} \mid \underline{\text{AgCl}} \mid \text{Ag}$ $E = -0.14 \text{ volt}$
 $\quad \quad \quad - \quad \quad \quad \rightarrow \quad \quad \quad +$
- (6) $\text{Ag} \parallel c_2\text{HCl} \mid \underline{\text{AgCl}} \mid \text{Ag}$ $E = 0.30 \text{ volt}$
 $\quad \quad \quad + \quad \quad \quad \leftarrow \quad \quad \quad -$
- (7) $\text{Ag} \parallel \underline{\text{AgCl}} \mid \text{Ag}$ $E = 0.42 \text{ volt}$
 $\quad \quad \quad + \quad \quad \quad \leftarrow \quad \quad \quad -$

The saturated potassium chloride solution takes out much of the potential difference between the solutions, but not all. Since the value for cell 3 is a little less than that for cell 2, we can say that the ionized-air gap takes out most of the potential difference and perhaps all. We cannot say that all the potential difference has been eliminated experimentally until the technique is improved to the point where we can measure with a sufficient degree of accuracy to examine solutions so dilute that we can calculate potential differences with the same degree of accuracy. We can show, however, that the measured results are consistent among themselves.

From cell 7 we have $\underline{\text{AgCl}} \mid \text{Ag} = 0.42$. From the difference between cells 5 and 6 we have $\underline{\text{AgCl}} \mid \text{Ag} = 0.44$, which is inside the experimental error. From cell 6 we have $c_2\text{HCl} \mid \underline{\text{AgCl}} \mid \text{Ag} = 0.30$, while the algebraic sum of Nos. 5 and 7 gives 0.28. On standing No. 6 changes slowly from +0.30 to -0.18, which is not far different from the value for No. 5 and indicates that the silver had been chloridized by vapor of hydrogen chloride from the solution.

As the most probable values for the present we take: $\underline{\text{AgCl}} \mid c_1\text{HCl} = 0.21$, $\underline{\text{AgCl}} \mid c_2\text{HCl} = 0.14$, and $c_1\text{HCl} \mid c_2\text{HCl} = 0.082$, which adds up to 0.152 instead of 0.162. By taking the value for No. 3 as 0.07 complete agreement could be obtained.

ZINC-COPPER CELLS

The copper sulfate and zinc sulfate solutions were made up to be 0.25 *M* (0.5 *N*) with an accuracy of about 1 per cent, and were kept in bottles with siphons. The cuprocyanide solution was made 0.25 *M* in cuprous cyanide and 2.5 *M* in sodium cyanide. The sodium zinc cyanide solution was made from sodium cyanide and zinc sulfate, and was approximately 0.1 *M* with respect to zinc cyanide and 1.0 *M* with respect to excess sodium cyanide.

The copper electrodes, cut from sheet copper and cleaned in nitric acid, were plated with copper from a cyanide bath, washed thoroughly in run-

ning tap water, and then rinsed in distilled water. The zinc electrodes were cut from a heavy sheet of zinc. After cleaning in hydrochloric acid solution, they were amalgamated by dipping in mercuric chloride solution and then rubbing with mercury until bright. The object of amalgamation is to prevent the formation of a coherent coating of zinc oxide. This effect is well-known and very striking in the case of amalgamated aluminum.

For the ionized-air cells both an inner and an outer electrode of each metal were provided, so that cross-checks could be made. The amalgamated zinc electrodes were reproducible within about 0.05 volt without great difficulty. The copper electrodes required more care; but approximately the same reproducibility was attained, provided the same general method of preparation was followed. A summary of the data is given.

- | | | |
|-----|---|--|
| (1) | Zn 0.5 N ZnSO ₄ 0.5 N CuSO ₄ Cu | $E = -1.106$ |
| | — → + | volts |
| (2) | Zn 0.5 N ZnSO ₄ sodium cuprocyanide Cu | $E = 0.32$ volt |
| | + ← — | |
| (3) | Zn sodium zinc cyanide sodium cuprocyanide Cu | $E = -0.13$ |
| | — → + | volt |
| (4) | Zn 0.5 N ZnSO ₄ sodium zinc cyanide Zn | $E = 0.45$ volt |
| | + ← — | |
| (5) | Zn Cu | $E = -1.05$ to -1.30 volts. |
| | — → + | The values obtained on the same days as the other measurements of this series were mostly grouped around -1.2 volts; but, previously and subsequently, more divergent values were found. |
| (6) | Cu 0.5 N CuSO ₄ Cu | $E = 0.02$ volt |
| | + ← — | |
| (7) | Cu sodium cuprocyanide Cu | $E = -1.4$ to -1.50^1 volts |
| | — → + | |
| (8) | Zn 0.5 N ZnSO ₄ Zn | $E = -0.03$ volt |
| | — → + | |

¹ When the first measurements on the Daniell cell with ionized air were made in 1935, the solutions were held on the electrodes with an agar gel. Re-design of the apparatus has made this unnecessary and all these measurements except No. 7 were made with only a thin film of solution covering the electrodes. When this was attempted with the cuprocyanide solution, cell 7 gave only about -0.5 to -0.7 volt and was very unsteady, presumably owing to oxidation of the cuprocyanide. Covering the electrode with filter paper, however, and wetting this with the solution caused the electrode to give the value tabulated. Complications, apparently due to some substance dissolved from the filter paper, will be discussed at a future time.

- (9) $\text{Zn} \mid 0.5 \text{ } N \text{ } \text{ZnSO}_4 \parallel \text{Cu}$ $E = -1.16 \text{ volts}$
 $\quad \quad \quad - \quad \quad \quad \rightarrow \quad \quad \quad +$
- (10) $\text{Zn} \mid 0.5 \text{ } N \text{ } \text{ZnSO}_4 \parallel 0.5 \text{ } N \text{ } \text{CuSO}_4 \mid \text{Cu}$ $E = -1.10 \text{ volts}$
 $\quad \quad \quad - \quad \quad \quad \rightarrow \quad \quad \quad +$
- (11) $\text{Zn} \parallel \text{sodium zinc cyanide} \mid \text{Zn}$ $E = 0.40 \text{ volt}$
 $\quad \quad \quad + \quad \quad \quad \leftarrow \quad \quad \quad -$

The values are not as consistent as those for the silver chloride concentration cells, though the discrepancy is not large. To make Nos. 4 and 11 consistent, we should have zinc 0.05 volt positive against zinc sulfate, whereas it is 0.03 volt negative according to No. 8, a discrepancy of nearly 0.1 volt. If we consider the potential difference between equimolecular zinc sulfate and copper sulfate solutions as zero and subtract 0.03 for zinc-zinc sulfate and 0.02 for copper-copper sulfate from the 1.106 for the cell as a whole, we get 1.056 volts for the contact potential between zinc and copper. This corresponds only with the lowest value given in No. 5; but it is quite probable that the copper was oxidized somewhat by the ionized air, in which case the observed values would be too high. This would apply also to No. 9.

As the most probable values for the present we may take $\text{Zn} \mid \text{ZnSO}_4$, $\text{ZnSO}_4 \mid \text{CuSO}_4$, and $\text{CuSO}_4 \mid \text{Cu}$ as approximately ± 0.1 volt, in which case the Volta potential for zinc and copper becomes $1.1 \text{ volts} \pm 0.1 \text{ volt}$.

Within the present limits of experimental error the electromotive force of the typical Daniell cell is due practically completely to the contact potential difference between zinc and copper. If we decrease the concentration of copper ions sufficiently, as by adding sodium cyanide solution to the copper sulfate solution, the direction of the current reverses (15) and the potential difference between copper and solution changes from approximately zero to approximately 1.4 to 1.5 volts, with the copper charged negatively. If we take $\text{Zn} \mid \text{sodium zinc cyanide} \mid \text{sodium cuprocyanide} \mid \text{Cu}$, the electromotive force is approximately zero (-0.13), the metal-electrolyte potential differences are approximately 1.45–0.32 volt (arithmetical sum is 1.8 volts), while the metal-metal potential difference is approximately 1.1 volts.

In Erskine-Murray's experiments (7), using a modified form of Volta's method with no ionized-air gap, the contact potential for zinc-copper would usually be from 0.7 to 1.0 volt, though occasional values as high as 1.2 volts were obtained (6). Similarly, Langmuir and others (20) report about 0.75 volt for the difference between the electron attractions of zinc and copper. The discrepancy between these results and ours is due to the fact that the physicists used pure zinc instead of amalgamated zinc. When we used pure zinc with an ionized-air gap we got values several tenths of a volt too low. The invisible oxide film is coherent in the case of pure zinc and not coherent in the case of amalgamated zinc.

When zinc or copper is oxidized intentionally, the oxidized metal becomes more cathodic. Erskine-Murray has even oxidized zinc to the point where it gave no potential difference against copper. We have confirmed his result by carrying the value down 0.8 volt with a less intensive oxidation. It is quite evident that no physicist who has studied Volta potentials has ever had a zinc surface that was not coated with a film, usually an oxide film. To that extent the chemists have always been right in their criticisms of the measurements of the physicists. Where the chemists slipped up was in not seeing that the presence of an oxide film on the zinc would decrease the apparent contact potential, and the presence of an oxide film on the copper would increase it. Not knowing the conditions under which an electromotive force is set up, they postulated that the oxidation of zinc in an air gap would set up a current.

Sir Humphry Davy (5) changed from the chemical theory to the contact theory in 1806 because "iron burnt in oxygen gas, properly connected with a condensing electrometer, gives no charge to it during the process. Nitre and charcoal deflagrated in communication with the same instrument do not by their agencies in the slightest degree affect the gold leaves." Ostwald (19) pointed out that there should be no electrification under these conditions, and yet he considered that the Volta fundamental experiment was merely an oxidation phenomenon.

The confusion that has arisen between the physicists and the chemists is brought out clearly in some comments by Kelvin on a letter by Lodge. Lodge said: "There is a true contact-force at a zinc-copper junction, which on a simple and natural hypothesis (equivalent to taking an integration constant as zero) can be measured thermoelectrically and is about one-third millivolt at 10°C. A voltaic force, more than a thousand times larger, exists at the junction of the metals with the medium [solutions] surrounding them; and in an ordinary case is calculable as the difference of the oxidation-energies; but it has nothing to do with the heat of formation of brass."

Kelvin said: "What would be the efficacy of the supposed oxygen bath in the experiments with varnished plates of zinc and copper? or in Erskine-Murray's experiment, described in his paper communicated last August to the Royal Society, in which metallic surfaces, scraped under melted paraffin so as to remove condensed oxygen or nitrogen from them, and leave fresh metallic surfaces in contact with a hydrocarbon, are subjected to the Voltaic experiment? or in Pfaff's and my own and Pellat's experiments with different gases, at ordinary and at low pressures, substituted for air? or in Bottomley's high vacuum and hydrogen and oxygen experiments above?"

"The anti-Voltaists seem to have a superstitious veneration for oxygen. Oxygen is entitled to respect because it constitutes fifty per cent of all the

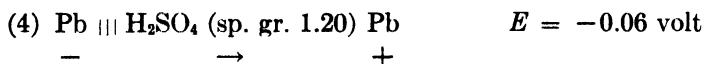
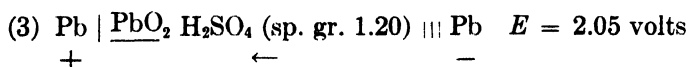
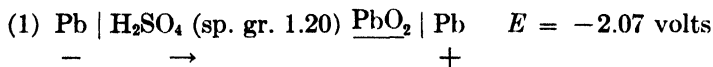
chemical elements in the earth's crust, but this gives it no title for credit as coefficient with zinc and copper in the dry Volta experiment, when there is none of it there. Oxygen has more affinity for zinc than for copper; so has chlorine and so has iodine. It is partially true that different metals—gold, silver, platinum, copper, iron, nickel, bismuth, antimony, tin, lead, zinc, aluminium, sodium—are for dry Volta contact-electricity in the order of their affinities for oxygen; but it is probably quite as nearly true that they are in the order of their affinities for sulphur, or for oxy-sulphion (SO_4) or for phosphorus or for chlorine or for bromine. It may or may not be true that metals can be arranged unambiguously in order of their affinities for any of these named substances; it is certainly true that they cannot be arranged *definitely and surely* in respect to their dry Volta contact-electricity. Murray's burnishing, performed on a metal which has been treated with Pellat's washing with alcohol and subsequent scratching and polishing with emery, alters the quality of its surface far more than enough to change it from below to above several metals polished only by emery; and, in fact, Pellat had discovered large differences due to molecular condition without chemical difference, before Murray extended this fundamental discovery by finding the effect of burnishing."

While we agree with Lord Kelvin's conclusion that there is a real potential difference between two metals in contact, we cannot endorse all of his arguments. Bottomley (3) found a value of a little over 0.74 volt for the Volta potential between zinc and copper. Reducing the pressure to less than 0.002 mm. had no effect on the measured potential difference, nor did the substitution of hydrogen for air. These experiments prove nothing nowadays, because the low pressure would not decompose a zinc oxide film and gaseous hydrogen would not touch it at ordinary temperatures. Erskine-Murray scratched a copper plate under melted paraffin wax so as to get a presumably clean surface, allowed the wax to cool, and found that there was little or no change relative to a plate exposed to air but not covered with wax. This sounds very convincing until one remembers that air is quite soluble in melted paraffin, 15 to 20 volume per cent, and that consequently the copper plate was always exposed to oxygen and undoubtedly always had an oxide film on it.

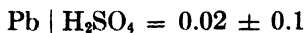
Kelvin lays special stress on the fact that the order of metals as determined by oxygen, chlorine, sulfur, etc., are much the same; but this does not prove anything. Unless special complexes are formed, the heats of reaction and the free energies will vary approximately in the same order. The question of the effect of burnishing and scratching is of no importance today, because we know that changing the crystal size and straining the crystals have definite effects on the potential differences at electrode surfaces.

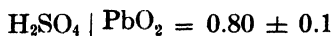
LEAD STORAGE CELL

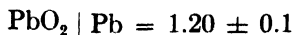
The lead electrodes were made from sheet lead. To prepare a peroxide electrode, a lead electrode was made anode in 20 per cent sulfuric acid with a current density of about 1 ampere per dm.² Almost at once it turned dark brown with a coppery sheen, and then oxygen was given off. After a few minutes the electrode was removed, rinsed well with distilled water, and dried quickly over a heater. It must not be allowed to stand wet more than ten or twenty minutes, otherwise the film breaks down. The peroxide film is purposely left thin to facilitate the removal of acid and water. When this was not necessary, a thicker film was prepared by forming the electrode. The ionized-air cells showed occasionally a marked tendency to change with time.



To make 1, 3, and 4 consistent, 4 should have been 0.02 instead of -0.06. The most probable values at present are:



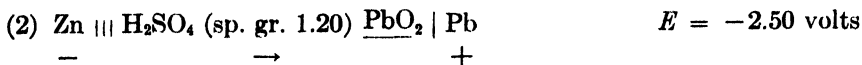
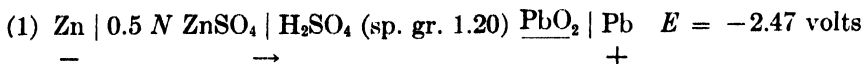
$$\rightarrow$$


$$\rightarrow$$


$$\rightarrow$$

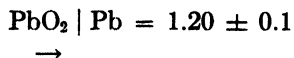
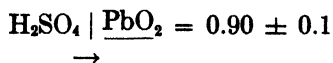
This makes the total for the cell 2.07, as it should be; but the data are not really anywhere near as accurate as this. There is always the probability of an oxide film on the lead.

To get away from this to some extent a few experiments were made with an amalgamated zinc anode in zinc sulfate.





This means in round numbers:



No matter what set of figures one takes, the peroxide electrode gives rise to practically all the electromotive force of the cell, and the potential differences on the two sides of the peroxide film are of the same general magnitude. That will undoubtedly remain true even though the absolute values be shifted.

PLATINUM-HYDROGEN ELECTRODE

It seemed probable that platinum in the presence of hydrogen would behave differently from platinum in air, contrary to what Bottomley and others believed. Consequently a few preliminary experiments were made to test this.

A smooth, bright-platinum inner electrode was used with silver, copper, and amalgamated zinc outer electrodes (prepared as before) as references. Tests showed that the potentials of zinc and of silver measured against copper were not affected appreciably by substituting ionized hydrogen for ionized air. The platinum was cleaned either by glowing in a flame or by treating with warm chromic-acid cleaning solution (bichromate and sulfuric acid).

The hydrogen was from a commercial cylinder and was, at first, passed through alkaline pyrogallol and concentrated sulfuric acid to purify it; but later, in order to avoid explosions, it was found necessary to pass it into the electrode chamber too rapidly to permit washing. No significant differences in the potentials were observed when purification of the hydrogen was discontinued. Behavior similar to that of a poisoned hydrogen electrode in a liquid solution was noticed on one occasion, but did not occur again.

To confine the hydrogen around the electrodes a copper box was made. In use, this was inverted on the desk top near the electrode and filled with hydrogen through a tube at the top. Then, with the hydrogen still flowing, it was picked up carefully and lowered quickly over the electrodes displacing the air. The excess hydrogen escaped round the bottom. This method was preferable to placing the copper box over the electrodes and

then passing in hydrogen at the top to displace the air downwards, since the latter procedure resulted occasionally in explosions, due apparently to catalysis at the platinum surface.

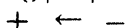
The reproducibility of cells with platinum electrodes is not very good as yet. We had hoped that the hydrogen cells would behave more consistently than they did, but the general results show up fairly well. It made little difference whether the platinum was activated by flaming or in a chromic-acid cleaning solution.

In the following data H denotes ionized hydrogen.

$$(1) \text{ Ag} ||| \text{ Pt} \quad E = -0.17 \text{ volt}$$



$$(2) \text{ Ag} | \text{ H} | \text{ Pt} \quad E = 0.83 \text{ volt}$$



The values in 1 and 2 are based on a single measurement each.

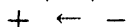
$$(3) \text{ Ag} ||| \text{ Cu} \text{ and } \text{ Ag} | \text{ H} | \text{ Cu} \quad E = 0.30 \text{ volt, the same in the two cases.}$$



$$(4) \text{ Cu} ||| \text{ Pt} \quad E = -0.76 \text{ volt}$$



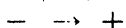
$$(5) \text{ Cu} | \text{ H} | \text{ Pt} \quad E = 0.35 \text{ to } 0.50 \text{ volt}$$



$$(6) \text{ Zn} ||| \text{ Pt} \quad E = -1.4 \text{ volts}$$



$$(7) \text{ Zn} | \text{ H} | \text{ Pt} \quad E = -0.33 \text{ volt}$$



These results are not consistent among themselves. Since we know that $\text{Zn}|\text{H}|\text{Cu}$ is about the same as $\text{Zn}|||\text{Cu}$ and that $\text{Zn}|\text{H}|\text{Ag}$ is about the same as $\text{Zn}|||\text{Ag}$, we conclude that ionized air and ionized hydrogen behave about alike with zinc, copper, and silver, whereas ionized hydrogen makes platinum 1.0 to 1.2 volts less noble. This is another way of saying that platinum activates hydrogen--which we know happens--whereas zinc, copper, and silver do not activate it appreciably under these conditions. Spiers (21) obtained very different values for iron platinum in air and in hydrogen, but he attributed this chiefly to changes in the iron. He may have been right in this, because his treatment was a bit heroic.

BEHAVIOR OF ALLOYS

In order to get a preliminary idea of how alloys might be expected to behave, a crude, synthetic alloy was prepared by covering a zinc electrode more or less completely with pieces of copper. These alloy substitutes replaced the zinc electrode in our standard Daniell cell and were also meas-

ured against copper with an ionized-air gap between. The two systems behaved entirely differently, rather to our surprise. In the solution the composite electrode gave low values for a short time and then came back approximately to the value for the Daniell cell. The composite electrode is a short-circuited cell and precipitates zinc on the copper. One measures, therefore, the potential due to the less noble phase in the alloy.

With the ionized-air gap against copper, the composite electrode gave a value nearly equal to that of zinc when the amount of attached copper was very small and nearly equal to that of copper when the zinc surface was covered nearly completely by copper. With the composite electrode and the ionized-air gap, there is no change in surface if we assume that oxidation is negligible under the conditions of the experiments, and consequently the observed electromotive force is a function of the nature and relative masses of the two phases in a binary alloy.

This explains why an electrode is so much more sensitive to polishing and scratching when determining the single-potential differences by Kelvin's methods than when the same electrode is in contact with a solution. If the scratching or polishing makes the surface more or less homogeneous, it will change the observed potential difference, whereas the electrode in solution changes only when one changes the less noble phase.

PASSIVE IRON

It was expected that we could measure the Kelvin single-potential difference between iron and passive iron, thereby getting an independent confirmation of our previous proof (2) that passive iron owes its peculiarities to an adsorbed film of the instable oxide, FeO_3 . To eliminate the effect of oxidation as much as possible, the iron electrode was amalgamated with sodium amalgam and the sodium washed out. The iron was made passive in concentrated nitric acid, sp. gr. 1.42, and was washed and dried carefully to avoid damaging the film. After the measurement, it was tested for passivity by dipping into nitric acid of sp. gr. 1.20.

Against amalgamated iron, iron which has stood in the air for several days after being cleaned, iron which has been made passive and dried carefully, active iron dried in the same way, and iron freshly cleaned in acid, rinsed and wiped dry, all give approximately the same values. They are approximately 0.1 volt cathodic. To make matters worse, a piece of iron which has been heated in the air until it has a thick film of oxide on it is approximately 0.6 volt cathodic to amalgamated iron. At present the Kelvin method gives no information in regard to passive iron. We do not know whether this is because the oxide film is too thin, too porous, or both. We do know that a thin film of oxide on zinc lowers the potential 0.3–0.4 volt, while a thick one may lower it 0.8–1.0 volt. We have also shown that an unspecified iron oxide film, presumably ferric oxide, will change the

Kelvin potential against iron 0.1–0.6 volt, perhaps more. More study of the oxide films is evidently called for.

SUMMARY

The general results of this paper are as follows:

1. Both Kelvin and Helmholtz evidently saw that a term for the Volta potential is included in the heat of reaction as determined by the thermochemist, though they seem not to have mentioned it specifically. The chemist has not been clear on this point because he has postulated that the Volta potential is negligible. Gurney (1932) is apparently the man who brought the matter into the open.

2. A pure zinc surface in air is always coated with a coherent film of oxide which makes the metal appear more noble. Amalgamated zinc does not form a coherent film on the surface. Since the physicists, from Volta down to the present, have not understood about amalgamated zinc, they have never had a surface corresponding at all to pure zinc.

3. Scratching a zinc or copper surface under molten paraffin is merely a beautiful gesture, because air is soluble in the hydrocarbon. A further proof is that the results thus obtained are those of the slightly oxidized metal.

4. By using amalgamated zinc we have been able to confirm the contention of Kelvin and of J. J. Thomson that an ionized-air gap removes most, and probably all, of the potential difference between the adjoining phases.

5. By putting in an ionized-air gap successively at each junction in a voltaic cell it is possible now to measure the Kelvin single-potential difference at that junction to at least ± 0.1 volt. There is no apparent reason why the measurements should not be made much more accurate.

6. In the ordinary Daniell cell, $\text{Zn}|0.5\text{ }N\text{ ZnSO}_4|0.5\text{ }N\text{ CuSO}_4|\text{Cu}$, practically all the electromotive force arises at the zinc-copper junction, the potential differences at the other junctions being each approximately zero.

7. On adding sodium cyanide to both sides of the ordinary Daniell cell the electromotive force may be dropped from 1.106 volts to 0.13 volts, in which case the arithmetical (not algebraical) sum of the metal-electrolyte potentials increases from approximately zero to approximately 1.8 volts, which is nearly double the Volta potential difference between the metals.

8. In the lead storage cell with sulfuric acid of sp. gr. 1.20, practically all of the electromotive force is developed at the lead peroxide electrode, the potential differences at the two sides of the peroxide film being roughly of the same order of magnitude.

9. The Kelvin single-potential difference for platinum-hydrogen and

platinum-air is apparently about 1.0-1.2 volts. The change from air to hydrogen has no marked effect with zinc, copper, and silver.

10. With two-phase binary alloys the Kelvin single-potential difference is a function of the nature and relative masses of the two phases.

11. It is not possible at present to get information about passive iron with an ionized-air gap.

12. We have used the term "Kelvin single-potential difference" because it is not yet known whether the ionized-air gap removes all the potential difference between the adjoining phases and gives the true or Volta potential differences.

13. The important thermodynamic developments by Helmholtz, Gibbs, Nernst, and Planck are not affected by these measurements. Their validity is the same now that it was before. The calculations of so-called solution pressures are now worthless, because they depended on the explicit assumption that the contact potential difference between metals was negligible.

REFERENCES

- (1) BANCROFT: *Trans. Am. Electrochem. Soc.* **9**, 13 (1906).
- (2) BANCROFT AND PORTER: *J. Phys. Chem.* **40**, 37 (1936).
- (3) BOTTOMLEY: *Brit. Assoc. Advancement Sci. Reports* **55**, 901 (1886).
- (4) BUTLER: *Chemistry & Industry* **4**, 3 (1926).
- (5) DAVY: *Collected Works*, **5**, 49 (1840).
- (6) ERSKINE-MURRAY: *Proc. Roy. Soc. London* **59**, 333 (1896).
- (7) ERSKINE-MURRAY: *Phil. Mag.* [5] **45**, 398 (1898).
- (8) ERSKINE-MURRAY: *Phil. Mag.* [5] **46**, 114 (1898).
- (9) GÖCKEL: *Wied. Ann.* **24**, 618 (1885).
- (10) GREINACHER: *Ann. Physik* [4] **16**, 708 (1905).
- (11) GURNEY: *Proc. Roy. Soc. London* **136A**, 379 (1932).
- (12) HELMHOLTZ: *Ueber die Erhaltung der Kraft*, p. 47 (1847).
- (13) HELMHOLTZ: *J. Chem. Soc.* **39**, 301 (1881).
- (14) KELVIN: *Phil. Mag.* [5] **46**, 114 (1898).
- (15) KÜSTER: *Z. Elektrochem.* **4**, 505 (1898).
- (16) LANGMUIR: *Trans. Am. Electrochem. Soc.* **29**, 125 (1916).
- (17) LODGE: *Phil. Mag.* [5] **49**, 368 (1900).
- (18) OSTWALD: *Elektrochemie*, p. 297 (1896).
- (19) OSTWALD: *Elektrochemie*, p. 334 (1896).
- (20) RIDEAL: *Trans. Faraday Soc.* **19**, 670 (1924).
- (21) SPIERS: *Phil. Mag.* [5] **49**, 70 (1900).
- (22) Cf. TRAUBE: *Ber.* **26**, 1473 (1893); HABER: *Z. physik. Chem.* **34**, 514 (1900).

SEDIMENTATION VOLUME, DILATANCY, THIXOTROPIC AND PLASTIC PROPERTIES OF CONCENTRATED SUSPENSIONS

H. FREUNDLICH AND A. D. JONES

*The Sir William Ramsay Laboratories of Inorganic and Physical Chemistry,
University College, London, England*

Received July 21, 1936

Concentrated paste-like suspensions of fine powders in liquids manifest certain properties, which depend strongly on the degree of packing. The rule given in table 1 was put forward, and was shown to hold in a few cases (2, 3). This rule was considered to be rather a rough guide, since factors such as particle shape, etc., were not taken into account. It would obviously be necessary to investigate the physical side of each of these phenomena more thoroughly, because very little is known about them. But, before doing so, it seemed desirable to compare the behavior of a large number of powders of different kinds to see whether the rule really was a first approximation to the truth, and to detect cases which might be specially fit for more exact investigation. This was the aim of the following paper.

The substances used, most of which are minerals, are listed in table 2. The objection could be raised that they might be impure, and that this would impair the results. We selected the minerals in as pure a condition as possible, and any obvious foreign matter was removed; there were two mixtures,—chalk and Solnhofen slate. In addition, the results seemed to show that small amounts of impurities, less than 1 per cent or so, did not change fundamentally the properties under investigation.¹ Minerals have, on the other hand, several advantages. Many of them are highly insoluble, and they are harder than the solid products of the same constitution chemically which have been precipitated from solution.

A thixotropic and plastic behavior was observed only if the solid particles in the suspension were sufficiently fine. There should be present a fairly high percentage with a diameter of between 1 and 10 μ .

The original substances were first coarsely ground in a porcelain mortar, or in an iron percussion mortar in the case of hard substances. These powders were then ground to the correct size, in most cases in a porcelain

¹ Cf. the discussion on the behavior of different forms of calcium carbonate, at the end of this paper.

ball-mill, containing 55 hard porcelain balls of a diameter of 1.50 cm.; generally, about 200 g. of the coarse powder was put into the mill with 0.25 l. of water, the lid then clamped on, and the whole lot rotated at 60 to 80 R.P.M. until the powder was sufficiently fine, as determined by sedimentation. Very hard substances, such as quartz and rutile, were powdered finely in a mechanical agate mortar, because they would be contaminated to a large extent with porcelain powder if the ball-mill were used.²

The powders were fractionated by sedimentation in water, and the fraction with particles of diameters between 1 and 10 μ was selected for the experiments. In some cases the particles stuck together in water; then they sedimented in a clear line, either because they were actually homodisperse, or because the larger particles formed a network which enmeshed the smaller ones, and caused the whole lot to sediment together. Since such powders could not be fractionated under these conditions, they were ground in the ball-mill until the rate of fall of the sedimenting level corresponded to the correct particle size. The diameter of the particles, as cal-

TABLE 1
Properties of paste-like suspensions

PROPERTIES DEPENDENT UPON CLOSE PACKING	PROPERTIES DEPENDENT UPON LOOSE PACKING
Small volume of sedimentation	Large volume of sedimentation
Dilatancy	No dilatancy
No thixotropy	Thixotropy
No plasticity	Plasticity

culated from the sedimentation velocity, according to Stokes' law, agreed in a satisfactory way with the value observed in microscopic measurements.

Four liquids were used,—pure water, and *N* aqueous solutions of hydrochloric acid, sodium hydroxide, and sodium chloride. The measurements with the electrolyte solutions were clearly not sufficient to show how changes in the nature and concentration of the electrolytes influenced the properties under investigation, but it seemed desirable to use these solutions in order to gain some idea of the kind and amount of the change caused by the presence of electrolytes.

² This contamination might falsify the results also with other powders, especially those of harder substances. To test this a sample of a fairly hard substance, hematite (hardness 5.5–6.5 in Mohs' scale) was ground to the same size (about 5 μ diameter) in the ball-mill, another in the agate mortar. The two samples behaved identically as to dilatancy, thixotropy, and plasticity. Hematite pastes are not dilatant, but are strongly thixotropic and plastic; a small difference as to sedimentation volume was insignificant. It was shown further that finely powdered porcelain could not be expected to behave in a very active way as an impurity. Its pastes turned out to be closely packed; they were dilatant, but neither thixotropic nor plastic.

TABLE 2
Description of substances studied

SUBSTANCE	CHEMICAL COMPOSITION	HARDNESS	CRYSTALLINE STRUCTURE
1. Diamond	C	10	Cubic
2. Graphite	C	0.5-1	Hexagonal
3. Jet	(C)*		Amorphous
4. Corundum	Al ₂ O ₃	9	Hexagonal
5. Hematite	Fe ₂ O ₃	5 5-6 5	Hexagonal
6. Pyrolusite	MnO ₂	2-2 5	Rhombic
7. Litharge	PbO	5-5 5	Amorphous
8. Quartz	SiO ₂	7	Hexagonal
9. Rutile	TiO ₂	6-6 5	Tetragonal
10. Titanium dioxide	TiO ₂		Tetragonal
11. Vanadium pentoxide	V ₂ O ₅		Rhombic
12. Tin pyrites	SnS ₂ ·Cu ₂ S·FeS	3-4	Tetragonal
13. Galena	PbS	2-3	Cubic
14. Mosaic gold	SnS ₂		Hexagonal
15. Fluorspar	CaF ₂	4	Cubic
16. Barytes	BaSO ₄	3-3 5	Rhombic
17a. Gypsum (oven-dried)	CaSO ₄ ·xH ₂ O†	1 5-2	Rhombic
17b. Gypsum (air-dried)	CaSO ₄ ·2H ₂ O	1 5-2	Monoclinic
18. Selenite	CaSO ₄ ·2H ₂ O	1 5-2	Monoclinic
19. Calcium carbonate (pure)	CaCO ₃		Hexagonal
20. Aragonite	CaCO ₃	3 5-4	Rhombic
21. Iceland spar	CaCO ₃	3	Hexagonal
22. Limestone	CaCO ₃	3	Hexagonal
23. Marble	CaCO ₃	3-4	Hexagonal
24. Mica (muscovite)	Complex silicate	2 5-3	Monoclinic
25. Monax glass	Complex silicate	6	Amorphous
26. Porcelain	Complex silicate	7	Amorphous
27. Kaolin	Complex silicate	2-2 5	Monoclinic
28. Steatite	Complex silicate (H ₂ Mg ₃ Si ₄ O ₁₂)	1	Monoclinic
29. Chalk	CaCO ₃ , mixed with clay		Hexagonal
30. Solnhofen slate	CaCO ₃ , mixed with clay		Hexagonal

* Jet is an intermediate compound between wood and coal, formed from petrified wood under high pressure, and it contains vegetable structures. It is homogeneous, and contains carbon, some 8 per cent of water, and 20 per cent of hydrocarbons, which appear on distillation. It shows a subconchoidal fracture, and is amorphous.

† After the gypsum had been ground to the correct size in water in the ball-mill, the excess water was removed by filtration and half of the residue was dried at about 90°C. in a steam oven, and half by exposure to the air for several days. The oven-dried sample had lost some of its water of crystallization.

SEDIMENTATION VOLUME

This was determined by allowing a known weight of powder to sediment uniformly in a known volume of water or aqueous solution, in graduated tubes having an internal radius of 0.58 cm., calibrated in cubic centimeters

up to 20 cc., and fitted with ground glass stoppers. The weight of the substance taken, in all cases, was that weight, as calculated from the density of the material, which had the same volume as had 3.00 g. of quartz, i.e., 1.13 cc. By using a constant volume, the results for the individual substances could be directly compared.

The tubes were first carefully cleaned. Then a small known volume of the liquid was poured in, and this was followed by the weighed quantity of the powder, and finally the rest of the liquid was admitted, and the whole lot shaken up until all the solid was in suspension. When the sediment had commenced to settle, and a layer of clear liquid had appeared on the surface, the solid which remained on the walls of the tube above the liquid was pushed down into the liquid by means of a rubber plunger. Then the tube remained undisturbed for at least twenty-four hours, and the volume of the sediment was read at the end of that time. The sediment was shaken into suspension again after this, and the experiment repeated until the sedimentation volume had reached a constant figure.

The sedimentation volume proved to be a most intricate phenomenon, depending strongly upon many factors; it evidently needs a thorough examination. The absolute value of the volume of sedimentation was less in wider tubes, and, in consequence, all the tubes had to be of the same internal cross section, in this case, 1.06 sq. cm., and of constant bore. It also depended, to a certain extent, on the volume of the liquid; it decreased slightly as the volume of the liquid decreased below a certain limiting liquid volume, which in this case was about 9.0 cc., so that 15.0 cc. of liquid was used in all cases, in order to be well above this limiting volume.

In many cases, as the determinations were repeated, the sedimentation volumes decreased gradually until the final value was reached. This was probably due to the removal of entrapped air by repeated shaking. This behavior, or when there was only a very small change at all, was considered to be the normal behavior. An increase in sedimentation volume which was observed in a number of cases was anomalous, and most likely due to a chemical action between solid and liquid.

VELOCITY OF SEDIMENTATION

Measurement of the sedimentation volume naturally led to a determination of the velocity of sedimentation, this being obtained by observing the limiting line between sediment and clear liquid a short time after shaking, and at intervals of a few minutes until there was practically no further fall; the time for the fall of the majority of particles was from two to three hours. Sedimentation velocity proved to be valuable in characterizing the behavior of the different suspensions.

With many substances, the sedimentation volume decreased markedly

if the tube was rolled to and fro between the palms of the hands after the solid had settled, and the particles allowed to settle without any further shaking. The standard time of rolling was 30 sec., the time of settling was, as before, about twenty-four hours, and this procedure was repeated until a constant volume was reached. A strong decrease, more than 25 per cent, was only observed with particles which were expected to be anisometric, i.e., plates or needles; for instance, mosaic gold in water (decrease 33 per cent), mica in water (decrease 40 per cent), and graphite in *N* hydrochloric acid solution (decrease 30 per cent). So the effect was probably due to the fact that the particles were oriented by the gentle movement. They were able to settle after orientation to a smaller sedimentation volume, the plates lying like sheets of a book on each other, while so long as they were lying irregularly, they enclosed a much larger volume of liquid, as was the case when they settled at random without being oriented (9).

DILATANCY

Dilatancy (8) was investigated only in a qualitative way, by mixing known amounts of the powders and liquids in a small basin into pastes, and observing the effect of a disturbance with a spatula. Normal or strong dilatancy was shown, for example, by a mixture of 5.0 g. of quartz and 2.25 cc. of water. This paste, if left to itself, appeared quite fluid, but when it was disturbed with a spatula, it immediately became dry and very resistant to the spatula. It was extremely difficult to pick up a portion of the paste on the spatula, but, once there, it became fluid again, and ran off in the manner of a treacly liquid. After the disturbance, if the paste was left alone again, it rapidly became liquid, and this could be accelerated by tapping the basin.

Non-dilatant pastes showed no change in consistency when they were disturbed with a spatula. No liquid exuded when they were spread out, nor when they were left to themselves, nor when the basin was tapped.

An intermediate behavior was observed between these extreme cases in a number of pastes, best described as a passive or weak dilatancy. The pastes concerned did not show any obvious change in consistency on mechanical treatment, nor did liquid exude when they were left to themselves, or at least, this happened very slowly. But when the vessel containing the paste which had been mixed with the spatula was gently tapped, liquid was soon seen to come out in quantity.

THIXOTROPY

Thixotropy was also observed in somewhat of a qualitative fashion, in a tube 18.0 cm. long and 0.93 cm. in internal diameter, fitted with a ground glass stopper. A series of pastes of increasing liquid concentrations was

made, beginning, frequently, with a mixture of 3.0 g. of the solid powder and 1.0 cc. of liquid, and the liquid content was increased in increments of 0.25 cc. at a time.

For each thixotropic paste, there was a region of concentrations where the mass became liquid on shaking, but solidified when left to rest. With a certain minimum amount of liquid, the paste could not be heard or felt to move when shaken; the only change was a change in its position in the tube before and after shaking. This concentration of solid was taken as the upper limit of the thixotropic region. As more liquid was added, the state was reached where the paste could be heard to flow when the tube was shaken, but it solidified immediately after shaking ceased. With still more liquid, the time of solidification became finite, and increased gradually; determinations ceased after it had reached ten minutes. The lower limit of the thixotropic region was generally chosen as that when the time of solidification was about a minute or so. On adding an excess of liquid, the paste did not solidify at all, but separated into two phases on standing.

In non-thixotropic pastes, the liquid masses did not solidify at all. As soon as the amount of liquid was sufficiently large, generally the whole mass flowed down when the tube was inverted, and the liquid separated from the solid when the tube was allowed to remain undisturbed, the sediment not being thixotropic. In some cases, mostly with coarser powders, when the tube was inverted, the solid remained as a hard clod at the top, and clear liquid ran down the walls of the tube.

Quite a number of pastes were found to be rheopectic, that is, they solidified more quickly if they were subjected to a regular gentle motion, as, for instance, by tapping the tube on the bench, or by rolling it to and fro between the palms of the hands. Rheopexy could only be observed in a region of concentrations where the time of thixotropic solidification was fairly long.³

PLASTICITY

Plasticity has not, so far as we know, been determined by any standard method. In order to compare plasticity with the other properties under consideration, an isothermal method of characterizing plastic behavior was essential. The method used was practically identical with that used for investigating flow pressure (6). The pastes were pressed against a disc, through the center of which was a small hole. The shearing took place at the hole. If the paste issued from the hole unchanged and well deform-

³ In some pastes a stable foam was formed, which was liable to cause apparent thixotropy and rheopexy by preventing the liquid part from flowing in the tube. This foam could be broken by a gentle tap on the outside of the tube, and then it could be seen whether thixotropy or rheopexy existed or not.

able, it was plastic;⁴ it was not plastic if it was changed in any way by the shearing forces.

This "plastometer" is shown in figure 1. The brass cylinder, AA, 7.6 cm. long, and 1.91 cm. in internal diameter, was fitted with a brass screw cap B at one end, to which was attached an inextensible rubber tube to convey the air pressure from a cylinder of air; and with another cap C on the other end with a hole in its center, 0.91 cm. in diameter. The jet, abcd, was housed in a piece of brass, whose vertical cross section was T-shaped, and which fitted through the hole in C, and could be clamped tight by screwing C on to the cylinder, and an air-tight joint obtained by interposing a lead washer. The jet was 0.16 cm. in diameter, drilled centrally and ground smooth with emery paste; the top, ab, was slightly counter-sunk, and the bottom edges were rounded off, else the threads tended to

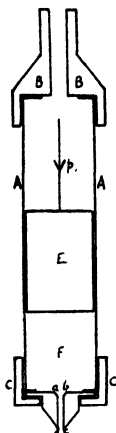


FIG. 1 The plastometer

curl up and stick to the brass and so form a loop instead of a nice straight thread. It was found necessary to communicate the air pressure to the paste by means of a brass piston E, of weight 60.6 g. The paste was put into the space F.

Air pressure was applied on to the piston from a cylinder of compressed air. The pressure was controlled by means of a reducing valve on the cylinder. Pressure was measured by means of a simple mercury manometer in centimeters of mercury, and all pressures are given as such. This valve also controlled the rate of rise of pressure.

The requisite amounts of liquid and powder were mixed in a small basin

⁴ We would thus agree with the following definition of plasticity: "Plasticity is that property which enables a material to be deformed continuously and permanently without rupture during the application of a force which exceeds the yield value of the material" (H. Wilson, *Ceramics; Clay Technology*, p. 55. New York (1927).)

with a flat spatula for a measured time, usually 30 seconds, and the homogeneous paste was transferred to the cylinder, also by means of the spatula, in a measured time, again usually 30 seconds. Then the cylinder and its ends were screwed together. After noting whether the weight of the piston alone was sufficient to cause any extrusion, pressure was applied slowly. The reducing valve was opened slightly to give a rate of rise of pressure of 1 or 2 cm. per minute, and this was continued for a few centimeters rise. Then the pressure was allowed to rise more quickly, and so on, in stages, always keeping the rate constant for a few centimeters rise before the next stage, and observing the effect of the pressure on the paste, until the final pressure rise of from 50 to 70 cm., which took place at about 60 cm. per minute.

TABLE 3
Behavior of a plastic paste of chalk

EXPERIMENT	PRESSURE	RATE OF RISE OF PRESSURE	RESULT	THREAD LENGTH
	cm.	cm. per minute		cm.
No. 1. 5 g. of chalk was mixed with 2.0 cc. of water by means of a flat spatula, in a small basin, for 30 sec., and transferred to the cylinder in 40 sec.	0		Nothing	
	1-3	1	Threads	1-2
	3-6	1-2	Threads	2-3
	6-10	6	Threads	3-4
	10-20	20	Threads	5-6
No. 2. 5 g. of chalk was mixed with 2.0 cc. of water by means of a flat spatula, in a small basin, for 30 sec., and transferred to the cylinder in 40 sec.	0		Nothing	
	1-2	1	Threads	1-2
	2-3	2	Threads	2-3
	3-9	7	Threads	3-5
	9-22	24	Threads	6-7

In each experiment all the paste was expressed.

If the paste was plastic, the mass was extruded in threads, which broke off as soon as they had reached a certain well-defined length. This length was measured on a scale below the jet.

Table 3 gives an example of the behavior of a plastic paste of chalk.

The measurements on the plasticity of these pastes were remarkably reproducible, provided that the above-mentioned precautions were taken.

The behavior of the pastes in this plastometer classified them very definitely and very simply into three groups: (i). *Plastic pastes*, which were extruded in threads of characteristic lengths. *Non-plastic pastes*, in which the extrusion took the nature of: (ii). Drops of clear liquid, there being left in the cylinder a hard and rather dry cake of the solid powder. (iii). Sticky or pasty drops, consisting of a mixture of the solid and liquid phases, containing an excess of liquid compared with the original mixture.

The rule mentioned above was found to hold for a great number of pastes.

Firstly, there are the cases agreeing with close packing; these are the suspensions which showed a small sedimentation volume, generally less than 4.0 cc. for the standard amount of substance (cf. page 1229), normal dilatancy, no thixotropy, and no plasticity, the extrusion in this case being sticky

TABLE 4

Sedimentation volumes in cubic centimeters of closely packed pastes which are not thixotropic

SUBSTANCE	LIQUID PHASE			
	Water	N HCl	N NaOH	N NaCl
Jet	4 0	4 6		4 6
Corundum		3 75		
Quartz	2 0	2 7		
Vanadium pentoxide	3 35			
Fluorspar	3 1	2 1	3 1	3 2
Monax glass	2 0	2 65		
Porcelain	2 0	2 7	3 65	3 4

TABLE 5

Sedimentation volumes in cubic centimeters of loosely packed pastes, which are strongly thixotropic and plastic

SUBSTANCE	LIQUID PHASE			
	Water	N HCl	N NaOH	N NaCl
Graphite	6 55	6 3	7 1	6 6
Jet			10 4	
Hematite	7 3	5 85	8 3	9 5
Titanium dioxide	9 6	7 0	10 1	9 75
Vanadium pentoxide		8 6		
Tin pyrites	7 55	10 6	5 4	7 5
Galena	8 8	8 8		5 95
Kaolin	6 3	6 5	6 8	7 4
Chalk			9 5	5 9
Solnhofen slate	5 9		11 2	5 9

drops of liquid. (The figures in the ensuing tables are the final volumes of sedimentation in cubic centimeters, previous to any intentional orientation.) The pastes shown in table 4 belong to this group.

Then there are cases agreeing with loose packing; these are the suspensions which showed a large sedimentation volume, generally greater than 6.0 cc., no dilatancy, strong thixotropy over a broad range of concentrations (for instance, thixotropic pastes of graphite in water contained from

32 to 52 per cent of solid and thixotropic pastes of hematite in water from 38 to 67 per cent of solid), and plasticity, the paste being extruded in well-defined long threads. To this group, the pastes listed in table 5 belong.

In addition to these cases in which the rule holds in its entirety, a number of examples were found where portions of the rule held quite strictly; generally, the properties connected in these cases were correlated in one direction only, and could not be reversed:

(1). There was practically no case of normal dilatancy which did not correspond to a small volume of sedimentation, that is, less than 4.0 cc. In this respect, there may be added to the pastes mentioned in table 4, those in table 6. These differ from those in table 4 by being weakly thixotropic; the range of thixotropy for corundum in water was from 63 to 67 per cent of solid, and that for Monax glass in *N* sodium chloride was from 57 to 63 per cent of solid. These pastes were not plastic.

TABLE 6

Sedimentation volumes in cubic centimeters of closely packed pastes which are dilatant, but also weakly thixotropic⁵

SUBSTANCE	LIQUID PHASE			
	Water	<i>N</i> HCl	<i>N</i> NaOH	<i>N</i> NaCl
Diamond.....	4 1	3.2		
Corundum.....	4 45		4 4	4.15
Quartz.....			3.4	3.3
Monax glass.....			3 5	3.5

The reverse does not hold true. Pastes with a very small volume of sedimentation need not show normal dilatancy; they may be passively dilatant. Examples of this are aragonite in water and *N* sodium chloride solution, and marble in water and *N* sodium chloride solution (see table 9).

(2). Suspensions which showed a large volume of sedimentation were also thixotropic. Examples are those in table 5, and to these, those in table 7 can be added. Table 7 contains pastes which have a large volume of sedimentation and, correlated with it, strong thixotropy, but which are

⁵ Litharge (in water and in sodium hydroxide solution) and rutile (in all four liquids) have probably to be added to this group. They both show certain anomalies. With litharge the volume of sedimentation is rather large (5.6 and 6.4, respectively), but as the latter increases in course of time, its behavior is anomalous and would need further investigation. Rutile in water is partly peptized, the sediment consisting of a brown layer. This is most likely an iron compound, and this impurity may be the reason why rutile pastes show no dilatancy, though this ought to be expected on the ground of their behavior as to the other properties. Titanium dioxide, as it is used for technical purposes and consisting of anatase, gives pastes which are very loosely packed (cf. table 5).

nevertheless passively dilatant and not plastic. In several cases the behavior of the sedimentation volume was anomalous; it increased markedly on repeating the experiment, but this was most likely due to some chemical reaction. This is obvious with the oven-dried gypsum. But this fact does not weaken the force of the argument that a large sedimentation volume favors thixotropy. (In table 7 the values given for the sedimentation volumes are the maximum values obtained.)

(3). Pastes which were markedly plastic were invariably thixotropic; they were also not dilatant. Table 8 contains pastes of this kind, but they do not fit into table 5 because the sedimentation volumes were medium or small.

TABLE 7

Sedimentation volumes in cubic centimeters of loosely packed pastes which are strongly thixotropic, passively dilatant, and not plastic

SUBSTANCE	LIQUID PHASE			
	Water	N HCl	N NaOH	N NaCl
Mica	8 45	8 5	8 25	8 0
Gypsum (oven-dried)	7 5	6 9		
Pure CaCO_3			7 05	
Iceland spar.	6 7		8 4	7 1
Galena.			10 9	

The extent of the thixotropic range for the suspensions cited in tables 7 and 8 was hardly less than that for the pastes in table 5, except that for mica it was decidedly smaller. Some examples are:

Substance	Per cent solid in thixotropic pastes
Mica	37-43
Gypsum (oven-dried)	41-60
Iceland spar.	50-67
Pyrolusite	60-71
Chalk	48-63

The liquid in all cases was water.

Here again, assertions 2 and 3 may not be reversed, as already follows from tables 7 and 8. Many pastes were thixotropic, although they had a small volume of sedimentation, as appears from table 8, and further examples are again aragonite and marble, mentioned above and in table 9; many pastes were also thixotropic but not plastic (table 7).

Pastes of the latter kind were numerous and rather characteristic; in table 9 are given pastes which unite these properties. The sedimentation volume was medium or small, that is, between 3.4 and 6.5 cc.; the pastes

showed passive dilatancy, distinct thixotropy, and no plasticity, clear liquid being pressed out of them.

Of these suspensions, gypsum (air-dried sample) has a fairly wide thixotropic range in water, 46 to 67 per cent solid, but the rest showed quite a limited range, for instance, mosaic gold in water, 52 to 60 per cent solid, and aragonite in water, 60 to 67 per cent solid.

The rule under discussion obviously simplifies matters too strongly. The following points have still to be considered.

TABLE 8

Sedimentation volumes in cubic centimeters of strongly plastic pastes which are also strongly thixotropic^a

SUBSTANCE	LIQUID PHASE			
	Water	N HCl	N NaOH	N NaCl
Pyrolusite.....	4 6	4 4	4 4	4 6
Barytes	3 1	2 8	3 4	3 1
Selenite	5 5	4 75	3 5	4 3
Chalk	4 45			

TABLE 9

Sedimentation volume in cubic centimeters of thixotropic pastes which have a medium or small volume of sedimentation, and which are passively dilatant and not plastic

SUBSTANCE	LIQUID PHASE			
	Water	N HCl	N NaOH	N NaCl
Mosaic gold.....	6 0	5 2	4.8	5 8
Gypsum (air-dried)	5 3	5 9	4 7	4.8
Gypsum (oven-dried)			5.5	6 35
Pure CaCO ₃	5 3			5 4
Limestone	5 3		6.4	5.6
Aragonite.....	3 65		5 75	3.4
Marble	3 4		4 55	4.2

In order that the pastes should show normal dilatancy, the particles should be quite independent of each other; then they are able to return spontaneously to the state of closest packing after they have been displaced. Particles of pastes with normal dilatancy (tables 4 and 6) are

^a Steatite must probably be added to this group. Its sedimentation volume could not be determined with certainty, owing to the very stiff foam which was formed and could not be broken. Thé plasticity measurements were also not well defined, obviously owing to the poor wettability of the powder. Pastes of selenite also gave only with high pressures well-defined threads when plasticity was measured

indeed very independent of each other. This can be seen in their behavior in the liquid medium under the microscope. They move about independently, and there is no attraction between them; if they come to rest by collision with each other, a slight disturbance can separate them and set them in motion again.

The independent nature of the particles belonging to this group of pastes is also shown by their *velocity of sedimentation*. The particles settle quite independently, according to Stokes' law:

$$U = \frac{2}{9} ga^2 \cdot \frac{(\rho - \sigma)}{\eta}$$

U = velocity of fall, g = acceleration due to gravity, a = radius of particles, ρ = density of particles, σ = density of liquid, and η = viscosity of liquid. If the suspension is sufficiently homodisperse, a , and thus U , is constant.

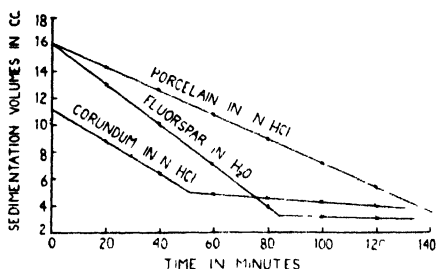


FIG. 2

FIG. 2 Sedimentation curves of porcelain, corundum, and fluorspar

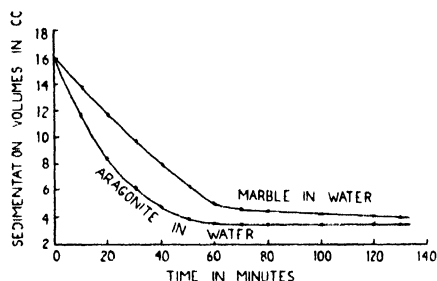


FIG. 3

FIG. 3. Sedimentation curves of marble and aragonite

In figure 2 the abscissa is the time in minutes, and the ordinate the volume of sedimentation in cubic centimeters, which is proportional to the space through which the particles have fallen. In the figure there are three curves for substances belonging to this group, porcelain and corundum in N hydrochloric acid solution and fluorspar in water. They are all straight lines approaching the abscissa; i.e., the tangent of the angle between the line and the abscissa, which is proportional to the velocity of sedimentation, is constant.

But the fact that a suspension has a small volume of sedimentation, that is, less than 4.0 cc., is not always an absolute proof that the particles are fully independent of each other, and that the packing is very close. Particles of aragonite and marble showed an anomalous behavior, in so far as they have a small volume of sedimentation in water and sodium chloride solution, but no normal dilatancy and a distinct thixotropy. It was found that their particles were not absolutely independent of each other when

they were observed under the microscope. They formed clusters, generally with a large particle in the center, and smaller particles stuck round it. These clusters appeared fairly independent of any neighboring clusters. Their curves of sedimentation were also not so simple as in the first case mentioned (cf. figure 3).

This tendency to form clusters was found with the particles of all pastes mentioned in tables 7 and 9. It is readily understood why these pastes showed passive dilatancy. The liquid in the system is probably associated in part with the clusters, and the rest is free; evidence for this is obtained from experiments with the plastometer, when in all cases with the pastes under consideration clear liquid was pressed out; that is, the free liquid was expressed, and this amounted to about 50 per cent of the original amount. In the passively dilatant pastes, the clusters are buoyed up by the liquid associated with them to such an extent that when determining dilatancy the clusters do not assume a very close packing, and no liquid appears

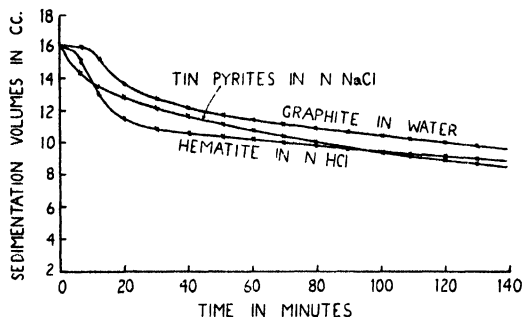


FIG. 4. Sedimentation curves of pastes which are not dilatant but strongly thixotropic and plastic

when the paste is left to itself. But when the vessel containing the paste is tapped, the solid phase is encouraged to separate from the liquid, and the free liquid appears on the surface. The clusters do not break up, and the phenomenon is reversible and may be repeated.

In pastes which are not dilatant but strongly thixotropic and plastic (tables 5 and 8), the particles aggregate to a much higher degree, as is shown in the microscope. They form a network through the system, and are all stuck together; there is no separation into clusters, and no motion.⁷ With systems of this kind there are very irregular curves of sedimentation velocity (cf. figure 4). These are the cases in which the particles cannot

⁷ This difference in behavior—coherent network of clusters and separate clusters, respectively—is also shown by “short” and “long” suspensions of carbon black in hydrocarbons (cf. R. O. Neal and G. St. Perrott, “Carbon Black, its Manufacture, Properties and Uses,” Bulletin 192 of the Bureau of Mines, p. 77 et seq., Washington (1922)).

be separated by fractionation. It is obvious that this strong aggregation favors the enclosure of large amounts of liquid, and thus causes a large volume of sedimentation, and thixotropy. There is indeed no exception to the rule that pastes with a large volume of sedimentation are always strongly thixotropic.

But the sedimentation volume need not be very large to cause a certain degree of thixotropy. If the sedimentation volume of the suspension is only a small amount greater than that of the most closely packed sediment, there appears a certain degree of thixotropy. Corundum, for instance, was not thixotropic in *N* hydrochloric acid solution, and its sedimentation volume was 3.75 cc.; but in water it was thixotropic and had a sedimentation volume of 4.45 cc. This small numerical increase of 0.60 cc. goes parallel with an increase in thixotropy.

The following observation on the variation of behavior of quartz particles in different liquid media assists this assertion. Quartz in water was not thixotropic. Quartz particles in water suspension on a microscope slide and viewed under a microscope were quite independent; they moved about, and gradually came to rest, and the smaller particles kept on moving long after the larger ones had ceased. By gently moving the cover glass, the system was disturbed and broken up, and it had to settle down all over again.

Quartz in *N* sodium hydroxide solution was thixotropic; quartz particles in this medium under the microscope moved about, but came to rest in a very much shorter time than in water, and there were no small particles left floating about. The system manifested attracting forces between the particles, and they seemed to cluster together. After the system had been disturbed by gently moving the cover glass, small particles rapidly made their way to the larger particles, and some could be seen to move with an acceleration, and attach themselves with a click.

This small change in behavior is sufficient to produce thixotropy; according to tables 4 and 6, the corresponding change in sedimentation volume for quartz is from 2.0 cc. in water to 3.4 cc. in *N* sodium hydroxide solution.

Here is then a further point, not expressed in the rule as originally specified, that although a large volume of sedimentation is always correlated with strong thixotropy, a large excess of liquid is not necessary to cause the latter phenomenon. Distinct thixotropic behavior may appear if the amount of liquid between the particles is not much larger than when the packing is very close. The volume of sedimentation need not be large. That is why a certain degree of thixotropy is so extremely frequent.

The dilatancy of these pastes and the manner in which they behave in the plastometer show that the liquid may be bound to the particles in a way varying strongly from paste to paste. If the liquid exudes spontaneously as in strongly dilatant pastes, it is bound very loosely, or only to a

rather small amount of the particles. The fact that, in the experiments on plasticity, the liquid is pressed out of the paste more or less easily proves that the liquid is readily separated from the particles. If the pastes show passive dilatancy, the liquid is part free, and part bound on to the clusters, and only the free liquid is squeezed out. Here the particles have a marked affinity for each other, they allow clear liquid to be expressed (tables 7 and 9), and the residue is a hard, rather dry cake. In the case of the pastes mentioned in tables 4 and 6, the affinity between the particles is small, with the result that the particles pass out with the liquid without keeping up a coherent structure, and the nature of the extrusion is pasty drops. In the plastic pastes (tables 5 and 8), the coherence is probably due to a mutual affinity both between the particles themselves and between the particles and the liquid.

It is a drawback in the discussion of this problem that the behavior of sedimentation volume is so very complex and not sufficiently known. Some points on this theme have been already mentioned; a further one should not be neglected. There is perhaps a certain tendency to assume that, at least in aqueous pastes, the electrical charge on the particles outweighs all other influences in determining the sedimentation volume.⁸ If the particles repel each other because they are markedly electrically charged or have a high ζ -potential, they remain independent and are able to glide over each other until they reach the closest packing. If the particles do not repel each other strongly, they stick to each other, that is, they are coagulated; in consequence they enclose large amounts of liquid, and this causes loose packing. The ζ -potential generally has a maximum in pure water, or in a small excess of OH^- ions, if the particles are naturally negatively charged, or of H^+ ions, if the particles are naturally positively charged; it decreases more or less strongly in solutions of neutral electrolytes, or in more concentrated solutions of acids and alkalis.

We actually frequently find a minimum of sedimentation volume in pure water, for instance, with the following substances,—jet, quartz, rutile, vanadium pentoxide, Monax glass, porcelain, pure calcium carbonate, limestone, Iceland spar, marble, mica, kaolin, steatite, chalk, and Solnhofen slate.

But there are also marked deviations from this normal behavior. A maximum of sedimentation volume in pure water was found in the case of the following substances,—corundum, mosaic gold, gypsum, selenite, and pyrolusite. A smaller volume in *N* acid solution was found with diamond and fluorspar, and a smaller volume in *N* sodium chloride solu-

⁸ The following reasoning is especially due to Ehrenberg (*Bodenkolloide*, p. 83 et seq., Dresden (1918)) and von Buzágh (*Kolloidchem. Beihefte* **32**, 114 (1930)), but they also take into account the influence of hydration.

tion was found for aragonite. This behavior needs thorough investigation. It is known that the volume of sedimentation may vary strongly with quartz in organic liquids where the electrical charge is of small importance (7, 5). Probably the question of solvation can also not be neglected in the case of aqueous solutions.

There appears to be no correlation between the ζ -potential of particles of different chemical nature, and their behavior concerning sedimentation volume, etc. For a number of particles, the ζ -potential was determined by measuring the electrophoretic velocity, using the well-known microscopic method.⁹ Particles whose volume of sedimentation was small and whose pastes were dilatant and not thixotropic had large values of ζ , e.g., quartz, -54 millivolts; diamond, -50; corundum, -58; but also in the case of particles which had a large volume of sedimentation, and which formed strongly thixotropic and plastic pastes, large ζ values were obtained, e.g., graphite, -52 millivolts; hematite, -35.

Most of the particles when observed under the microscope were isometric, i.e., roughly spherical or cubical in general outline. A number of substances were definitely anisometric. The particles were plates in mosaic gold, mica, graphite, kaolin, selenite, and steatite, and were needles in hematite; the particles of gypsum which had been dried in the oven recrystallized from the water in a few minutes into long needles also. The special shape of these particles was also shown by other properties. As was mentioned above, mosaic gold, mica, graphite, and to a certain extent, kaolin also, changed their sedimentation volumes strongly when the particles were oriented. In a number of dilute suspensions of mica, selenite, steatite, graphite, and mosaic gold, beautiful streaks were observed on stirring, a phenomenon which is known to be characteristic of suspensions of non-spherical particles (1). All pastes with anisometric particles were thixotropic. None showed normal dilatancy, but some (mosaic gold and mica) showed passive dilatancy, and were not plastic.

The hardness¹⁰ of the particles proved to be undoubtedly important in the determination of their behavior. Nearly all the substances having a strong tendency to be closely packed (tables 4 and 6) were hard; for example, diamond, 10; corundum, 9; quartz, 7; porcelain, 7; glass, 6, or were fairly hard, litharge, 5-5.5; and fluorspar, 4. Most of the substances whose pastes were loosely packed, and which, therefore, were thixotropic and plastic (tables 5 and 8) were soft, such as graphite 0.5-1; selenite 1.5-2; and steatite 1; or not very hard, galena 2-3; pyrolusite 2-2.5;

⁹ These experiments are perhaps not quite conclusive, as dilute suspensions are used, whereas all the properties we are investigating are determined with very concentrated suspensions.

¹⁰ Hardness is given in the scale of Mohs.

kaolin 2-2.5; and barytes 3-3.5. An exception was hematite, which was fairly hard (5.5-6.5), but whose pastes were loosely packed, thixotropic, and plastic.

A number of substances containing chiefly calcium carbonate but of different crystalline structure and of different degrees of purity were compared: pure calcium carbonate (hexagonal), aragonite (rhombohedral), limestone, Iceland spar, marble (all three hexagonal), chalk, and Solnhofen slate. The last two contained a certain percentage of impurities insoluble in hydrochloric acid, mainly of a clayey nature; they amounted to 1.23 per cent in chalk (average of two analyses), and to 5.89 per cent in Solnhofen slate (also two analyses). The fairly pure substances behaved very similarly; all showed passive dilatancy, distinct thixotropy, and no plasticity, pure water being extruded. The presence of clay in chalk and Solnhofen slate made the pastes of these two strongly thixotropic and plastic. The volume of sedimentation varied to a certain extent; it was of medium value with pure calcium carbonate, limestone, chalk, and Solnhofen slate, smaller with aragonite and marble, and rather larger with Iceland spar.

Pastes of gypsum are known to be strongly rheopectic (4). This was confirmed. We found further, that a number of other pastes closely related to gypsum were also rheopectic; for instance, pastes of selenite, all sorts of calcium carbonate (pure calcium carbonate, limestone, Iceland spar, marble, Solnhofen slate), and steatite. It is obvious that rheopecty can only be observed if the time of thixotropic solidification is sufficiently long, at least several minutes; rheopecty cannot be distinguished from thixotropy when the time of solidification is too short. In the way the range of thixotropy was determined, the range of rheopecty extends almost right up to the lower limit of thixotropy; for instance, the range of thixotropy in water for air-dried gypsum was from 46 to 67 per cent solid, and the range of rheopecty was from 40 to 46 per cent solid; for pure calcium carbonate in water, the range of thixotropy was from 54.5 to 67 per cent solid, and that of rheopecty from 50 to 52 per cent solid; for Solnhofen slate in water, the range of thixotropy was from 40 to 60 per cent solid, and that of rheopecty from 37.5 to 39 per cent solid. The lower limit of the thixotropic range was chosen so that the paste solidified spontaneously in a short time, one minute or so. Some of the more dilute pastes which fell into the rheopectic range also solidified spontaneously if left for a sufficiently long while, whereas in other pastes the two phases separated before the system solidified.

SUMMARY

In order to test the rule that close packing is joined to a small volume of sedimentation and to dilatancy, but not to thixotropy and plasticity,

whilst loose packing is joined to a large volume of sedimentation, to thixotropy and plasticity, but not to dilatancy, a large number of pastes, made of finely powdered solid substances (thirty different substances, mostly minerals) mixed with water or a few aqueous solutions, were investigated. Sedimentation volume, dilatancy, and thixotropy were determined by the methods generally applied: plasticity by a device similar to the one used in measuring flow pressure. Pastes were considered to be plastic if they were pressed out of a fine hole in coherent threads; in non-plastic pastes the liquid was pressed out in drops. The following results were obtained:

1. The rule holds in a large number of cases, but there are a number of exceptions in so far as thixotropy may be observed when the volume of sedimentation has medium values or is even rather small, and further when there is no marked plasticity.

2. There appears to be a strict correlation in so far as normal dilatancy is observed only when the volume of sedimentation is small and as plastic pastes are always thixotropic.

3. It was not sufficient to distinguish dilatant pastes from non-dilatant pastes. Some pastes showed the following behavior: they did not become distinctly harder when mechanically treated with a spatula and they did not let liquid exude when left to themselves. In so far they appear to be non-dilatant. But liquid did exude when the basin which contained the mechanically treated paste was gently tapped. This kind of dilatancy was called passive dilatancy.

4. There is a group of pastes uniting the following properties: generally a medium volume of sedimentation, passive dilatancy, distinct thixotropy, no plasticity.

5. The degree of independence of the particles is the best criterion for judging the probable behavior of their pastes. Independent particles have no tendency to unite into clusters when seen under the microscope; such particles always form systems according to the closely packed systems of our rule. If the particles are not independent, they are seen under the microscope to unite in clusters. These clusters may unite into continuous groups. Particles which are not independent always give pastes which are to a certain extent thixotropic, but they need not be plastic and their volume of sedimentation may even be fairly small.

6. The degree of independence makes itself felt also in the velocity of sedimentation. Fairly concentrated suspensions of independent particles of uniform size follow Stokes law for a long time of settling. If the particles have a tendency to cluster, a strong anomaly of the velocity of sedimentation is shown during the process of settling.

7. Markedly anisometric, especially plate-like, particles (mosaic gold, mica, graphite, etc.) always give thixotropic pastes.

8. Particles of very hard substances (diamond, quartz, corundum, etc.)

are always strongly independent, and therefore give systems with closely packed particles.

REFERENCES

- (1) DIESSELHORST, FREUNDLICH, AND LEONHARDT: *Elster-Geitel-Festschrift*, p. 453 (1915).
- (2) FREUNDLICH: *J. Soc. Chem. Ind.* **53**, 218T (1934).
- (3) FREUNDLICH AND JULIUSBURGER: *Trans. Faraday Soc.* **30**, 333 (1934).
- (4) FREUNDLICH AND JULIUSBURGER: *Trans. Faraday Soc.* **31**, 920 (1935).
- (5) HALLER: *Kolloid-Z.* **46**, 366 (1928).
- (6) Cf., for instance, KURNAKOW AND SHEMTSCHUSHNY: *J. Russ. Phys. Chem. Soc.* **45**, 1004 (1913); *Chem. Zentr.* **1913**, II, 1725.
- (7) OSTWALD, WO., AND HALLER: *Kolloidchem. Beihefte* **29**, 354 (1929).
- (8) REYNOLDS, OSBORNE: *Phil. Mag.* [5] **20**, 469 (1885); *Nature* **33**, 429 (1886).
- (9) VON BUZÁGH: *Kolloidchem. Beihefte* **32**, 124 et seq. (1930).

INDEX

- Absorption spectra of cephalin, lecithin, and selected antigens, 739
- Acid sodium oleate, sorption of, 277
- Activated charcoal, sorption of bromine and iodine by, 233
- Activation in flotation, 799
 - of redwood and ash-free sugar charcoal in a current of air, 603
- Activity coefficient of lithium chloride, 845
 - coefficient of potassium iodide, 845
 - coefficient of silver acetate in mixed solvents, 649
 - coefficients of lead bromate in solutions of electrolytes, 317
- Adsorbed ions, spectroscopic estimation of, 187
- Adsorption and diffusion in zeolite crystals, 223
 - at crystal-solution interfaces, 81
 - at crystal-solution interfaces, 177
 - at surfaces of red cells, 1063
 - by diatomaceous filters, 215
 - condenser and electromotive force, 1083
 - of complex ammonio ions by silica gel, 1055
 - of ions, 1183
 - of radon by glass, 419
 - of the heavier rare gases by mercury, 523
 - on chromite catalysts, 101
 - on ionic lattices, 1027
- Aging of mercuric sulfide and of zinc sulfide, 637
- Alcohols, sugar, effect of, on the dissociation of boric acid, 151, 927
- Alkali celluloses, x-ray spectrography of, 27
- Aluminum silicate, precipitated, cation-exchanging properties of, 747
- Amalgams, sodium, viscosity of, 709
- Ammonia, liquid, as a solvent, 581
 - d₃, radiochemical decomposition of, 155
- Amylophosphoric acid and proteins, coacervation of, 1191
- Angles, contact, effect of heat treatment on magnitude of, 881
 - contact, vertical-rod method for the measurement of, 881
- Asphalt, colloidal nature of, 1133
- Bacteriophagy, hypothesis concerning, 477
- Bayerite and böhmite, 47
- Bentonite precipitates, 1183
 - suspensions, gelation of, 1041
- Böhmite and bayerite, 47
- Boric acid, dissociation of, effect of certain sugar alcohols and their anhydrides on, 151, 927
- Brassicidic acid, mixtures of, with erucic acid, methyl brassidate, and ethyl brassidate, solubility relationships in, 905
- Bromine and water, mechanism of the photochemical reaction between, 613
 - sorption of, by activated charcoal, 233
- Cadmium sulfate, thermodynamic properties of, in water-ethyl alcohol solutions, 287
- Calcium carbonate, thermal dissociation of, 435
- Camphor, optical activity of, in alcoholic solutions, 853
- Capillaries, small, stream potentials and d.c. surface conductivities in, 207
- Carbon dioxide cleavage from dibromomalonic acid, 121
- Catalysis of ionic oxidation-reduction reactions by dyes, 1021
- Catalysts, chromite, adsorption on, 101
- Cataphoresis cell, cylindrical, optical difficulties with, 833
- Cathode, oxidation processes at, 769
 - polarization as a function of the current density in fused salts, 763

- Cation-exchanging properties of a precipitated aluminum silicate, 747
- Cell, cylindrical cataphoresis, optical difficulties with, 833
electrophoresis, for microscopic observations, 399
- Cellophane, ultrafiltration through, 1157
- Cellulose fibers, x-ray studies of crystallite orientation in, 343
membranes, bacterial, synthetic fibers from, 343
- Celluloses, alkali, x-ray spectrography of, 27
- Cephalin, absorption spectrum of, 739
- Chalcocite, action of potassium *n*-amyl xanthate on, 257
- Charcoal, activated, sorption of bromine and iodine by, 233
redwood and ash-free sugar, activation of, in a current of air, 603
- Chitin, x-ray diffraction studies of, 863
- Chitosan, x-ray diffraction studies of, 863
- Chromite catalysts, adsorption on, 101
- Coacervation of amylophosphoric acid and proteins, 1191
- Coagulation of sols by electrolytes, 1071
- Coal, bituminous, polymeric character of, 1103
- Coefficient, activity, of lithium chloride, 845
activity, of potassium iodide, 845
activity, of silver acetate in mixed solvents, 649
- Coefficients, activity, of lead bromate in solutions of electrolytes, 317
- Colloid chemistry, the phase rule in, 43
- Colloidal electrolytes, mixtures of, with uni-univalent salts, 493
solutions in concentrated electrolytes, 307
- Colloids, soil, vapor pressure-water content relations for, 195
- Compounds, addition, of phosphorous acid with organic compounds, 919
- Compressibilities, apparent, of solutes in solution, 461
- Conductance, surface, determination of, 715
- Constants, dielectric, of solutions of some organic acids in ethyl alcohol and benzene, 619
- Contact angles, determination of, from measurements of the dimensions of small bubbles and drops, 159, 169
angles, effect of heat treatment on magnitude of, 881
angles, vertical-rod method for the measurement of, 881
- Copper sulfate, diffusion of, in aqueous solution of sulfuric acid, 733
- Cosmic rays, penetration of, into fresh water lakes, 113
- Creeping of saturated salt solutions, 439
- Crystal habit of barium and lead nitrates, influence of dyes on, 81
-solution interfaces, adsorption at, 81, 177
- Cupric ferrocyanide sol, 1071
ion, diffusion coefficient and apparent radius of, in silica gels, 55
- Decomposition, radiochemical, of deutero-ammonia, 155
- Denaturation, influence of, on the spreading of proteins on a water surface, 361
- Deutero-ammonia, radiochemical decomposition of, 155
- Diatomaceous filters, adsorption by, 215
- Dibromomalonic acid, carbon dioxide cleavage from, 121
- Dielectric constants of solutions of some organic acids in ethyl alcohol and benzene, 619
- Diffraction studies, x-ray, of chitin, chitosan, and derivatives, 863
- Diffusion and adsorption in zeolite crystals, 223
coefficient of the cupric ion in silica gels, 55
of copper sulfate in aqueous solutions of sulfuric acid, 733
study of dyes, 1005
- Dilatancy of concentrated suspensions, 1217
- 2,4-Dinitrochlorobenzene, rate of reaction of, with primary amines, 669
- Dissociation of boric acid, effect of certain sugar alcohols and their anhydrides on, 151, 927
pressures, comparative method for measuring, 379
thermal, of calcium carbonate, 435

- Doughs, flour, physical properties of, in relation to bread-making qualities, 561
flour, rupture and flow in, 811
- Dyes, catalysis of ionic oxidation-reduction reactions by, 1021
diffusion study of, 1005
influence of, on crystal habit of barium and lead nitrates, 81
- Electrodes, glass and quinhydrone, comparison of, for the measurement of the activity of the hydrogen ion in sucrose solutions, 837
- Electrokinetic potentials, test of the identity of, 543
- Electrokinetics, 9
- Electrolytes, coagulation of sols by, 1071
colloidal, mixtures of, with uni-univalent salts, 493
concentrated, colloidal solutions in, 307
solutions of, solubility of lead bromate and its activity coefficients in, 317
- Electromotive force and the adsorption condenser, 1083
- Electrons, slow, electronic analysis of some surfaces by means of, 941
- Electrophoresis cell for microscopic observations, 399
U-tube method of measuring, 703
- Electrosmosis measurements with a glass slit, 543
- Emulsions containing milk fat, viscosity relationships in, 71
particle size and optical properties of, 1149
- Energy, free surface, of solids, 881, 889, 895
- Equilibrium, thermodynamic, in the gravitational field, 373
- Ethyl alcohol-glycerin-water system, 627
- Exchange, ionic, simple kinetic theory of, 501
- "Ferric hydroxide," colloidal, transference numbers of, 997
oxide precipitates, 1183
sulfate in aqueous solutions of other sulfates, 689
- Fibers, cellulose, x-ray studies of crystallite orientation in, 343
synthetic, from bacterial cellulose membranes, 343
- Films, unimolecular, of nerve proteins, 989
- Filters, diatomaceous, adsorption by, 215
- Flocculation of stannic oxide sols, 591
- Flotation agent, trimethylcetylammmonium bromide as, 661
physical chemistry of, 661, 799
- Flour doughs, physical properties of, in relation to bread-making qualities, 561
doughs, rupture and flow in, 811
- Furfural, production of, from xylose solutions, 133
- Gelation of bentonite suspensions, 1041
- Gel, silica, adsorption of complex ammonio ions by, 1055
- Gels, silica, diffusion coefficient and apparent radius of the cupric ion in, 55
silicic acid, studies on, 21
- Geometrical isomers, mixtures of, 905
- Glass, adsorption of radon by, 419
- Glycerin-ethyl alcohol-water system, 627
- Glycinin, isoelectric point of, 453
- Gravitational field, thermodynamic equilibrium in, 373
- Halogen compounds, reactivity of, 669
- Heat capacity of saturated sodium sulfate solution, 429
- Heats, specific, of the binary system methyl alcohol-toluene, 481
- Hide substance with hydrogen chloride and ammonia, 471
- Hydrogen bridges in ice and liquid water, 723
ion, activity of, in sucrose solutions, 837
- Hydrous oxide sols, constitution of, 1
- Indicators, oxidation-reduction, reduction of, 519
- Iodine, sorption of, by activated charcoal, 233

- Ionic exchange, simple kinetic theory of, 501
lattices, adsorption on, 1027
- Ions, adsorbed, spectroscopic estimation of, 187
- Iron, passive, the oxide film on, 37
- Isoelectric point of glycine, 453
- Kelvin single-potential differences, 1201
- Lanthanum, solubility of, in mercury, 333
- Lattices, ionic, adsorption on, 1027
- Lead bromate, solubility and activity coefficients of, in solutions of electrolytes, 317
sulfate, solubility of, in aqueous solutions of sulfuric acid at high concentrations, 303
- Lecithin, absorption spectrum of, 739
- Liesegang rings, formation of, in the presence of precipitates, 369
rings of manganese sulfide, 599
rings, quantitative analyses of, 645
- Lignin solutions, molecular properties of, 1113
- Liquid ammonia as a solvent, 581
- Liquids, surface tension of, application of the high-speed motion picture camera to research on, 973
- Lithium chloride, activity coefficient of, 845
- Manganese sulfide, Liesegang rings of, 599
- Mercuric sulfide, postprecipitation of zinc sulfide with, 779
- Mercury, adsorption of the heavier rare gases by, 523
solubility of lanthanum in, 333
- Metallic sulfides, solubilities and free energies of, 61
- Metals, effect of heat treatment in air on free surface energy of, 889
effect of heat treatment in a vacuum and in several gases on the free surface energy of, 895
- Method, U-tube, of measuring electrophoresis, 703
- Mixed crystal formation of zinc sulfide postprecipitated with mercuric sulfide, 637
- Molecular dimensions from viscosity studies, 125
properties of lignin solutions, 1113
weight changes of sulfur monochloride, 679
- Multiple electrode systems, polarization discharges in, 239
- Nerve proteins, unimolecular films of, 989
- Oxidation of toluene to benzoic acid, 531
potential of the system potassium molybdocyanide-potassium molybdicyanide, 247
processes at the cathode, 769
-reduction indicators, adsorbed, reduction of, 519
-reduction reactions, ionic, catalysis of, by dyes, 1021
- Oxide film on passive iron, 37
- Particle-size distribution in colloidal systems, new method for measuring, 1169
- Passive iron, the oxide film on, 37
- Phase rule in colloid chemistry, 43
- Phosphorous acid, addition compounds of, with organic compounds, 919
- Photochemical reaction between bromine and water, mechanism of, 613
- Plastic properties of concentrated suspensions, 1217
- Polarization, cathode, as a function of the current density in fused salts, 763
discharges in multiple electrode systems, 239
- Polymorphism, 89
- Positively adsorbed substances, surface spreading of, 835
- Postprecipitation of zinc sulfide with mercuric sulfide, 637, 779
- Potassium iodide, activity coefficient of, 845
n-amyl xanthate, action of, on chalcocite, 257
- Potential, oxidation, of the system potassium molybdocyanide-potassium molybdicyanide, 247
streaming, in small capillaries, 9

- Potentials, electrokinetic, test of the identity of, 543
stream, in small capillaries, 207
- Precipitates, physical character of, 1183
- Pressures, aqueous vapor and dissociation, comparative method for measuring, 379
- Proteins and amylophosphoric acid, coacervation of, 1191
nerve, unimolecular films of, 989
spreading of, on a water surface, 361
- Radiochemical decomposition of deuterio-ammonia, 155
- Radon, adsorption of, by glass, 419
- Rare gases, heavier, adsorption of, by mercury, 523
- Rays, solar and cosmic, penetration of, into fresh water lakes, 113
- Reaction, photochemical, between bromine and water, 613
- Reactivity of halogen compounds, 669
- Red cells, adsorption at surfaces of, 1063
- Rupture and flow in flour doughs, 811
- Salts, fused, cathode polarization as a function of the current density in, 763
uni-univalent, mixtures of colloidal electrolytes with, 493
- Sedimentation volume of concentrated suspensions, 1217
- Silica fluff, 413
gel, adsorption of complex ammonia ions by, 1055
gels, diffusion coefficient and apparent radius of the cupric ion in, 55
- Silicic acid gels, studies on, 21
- Silver acetate, solubility and activity coefficient of, in mixed solvents, 649
- Single-potential differences, Kelvin, 1201
- Soaps: electric charge effects and dispersing action, 821
- Sodium amalgams, viscosity of, 709
sulfate solution, saturated, heat capacity of, 429
- Soil colloids, vapor pressure-water content relations for, 195
- Sol, cupric ferrocyanide, 1071
- Solar rays, penetration of, into fresh water lakes, 113
- Sols, coagulation of, by electrolytes, 1071
direct examination of, by x-ray diffraction methods, 1095
hydrous oxide, constitution of, 1
stannic oxide, flocculation of, 591
- Solubilities and free energies of some metallic sulfides, 61
- Solubility of lanthanum in mercury, 333
of lead bromate and its activity coefficients in solutions of electrolytes, 317
of lead sulfate in aqueous solutions of sulfuric acid at high concentrations, 303
of silver acetate in mixed solvents, 649
relationships in mixtures of brassidic acid with erucic acid, methyl brassidate, and ethyl brassidate, 905
- Solutes in solution, apparent volumes and apparent compressibilities of, 461
- Solutions, colloidal, in concentrated electrolytes, 307
saturated salt, creeping of, 439
- Sorption of acid sodium oleate, 277
of bromine and iodine by activated charcoal, 233
- Specific heats of the binary system methyl alcohol toluene, 481
- Spectrography, x-ray, of alkali celluloses, 27
- Spectroscopic estimation of adsorbed ions, 187
- Spreading, surface, of positively adsorbed substances, 835
- Stannic oxide sols, flocculation of, 591
- Stream potentials in small capillaries, 207
- Streaming potential in small capillaries, 9
potential measurements with a glass slit, 543
- Sucrose solutions, activity of the hydro-gen ion in, 837
- Sugar alcohols, effect of, on the dissociation of boric acid, 151, 927
- Sulfides, metallic, solubilities and free energies of, 61
- Sulfur monochloride, molecular weight changes of, 679
- Surface conductance, determination of, 715

- Surface conductivities, d.c., in small capillaries, 207
spreading of positively adsorbed substances, 835
tension of liquids, application of the high-speed motion picture camera to research on, 973
- Surfaces, electronic analysis of, by means of slow electrons, 941
- Synthetic fibers from bacterial cellulose membranes, 343
- System ethyl alcohol-glycerin-water, physical properties of, 627
methyl alcohol-toluene, specific heats of, 481
potassium molybdocyanide-potassium molybdicyanide, 247
- Thermal dissociation of calcium carbonate, 435
- Thermodynamic equilibrium in the gravitational field, 373
properties of cadmium sulfate in water-ethyl alcohol solutions, 287
- Thixotropic properties of concentrated suspensions, 1217
- Thixotropy, studies in, 1169
- Tin vanadate as a catalyst in the oxidation of toluene to benzoic acid, 531
- Toluene, oxidation of, to benzoic acid, 531
- Transference numbers of colloidal "ferrie hydroxide," 997
- Trimethylcetylammonium bromide as a flotation agent, 661
- Ultrafiltration through Cellophane, 1157
- Vapor pressure, aqueous, comparative method for measuring, 379
- Viscometer, falling sphere, determination of wall correction for, 143
- Viscosity of sodium amalgams, 709
relationships in emulsions containing milk fat, 71
studies, molecular dimensions from, 125
- Volumes, apparent, of solutes in solution, 461
- Water, hydrogen bridges in liquid, 723
- X-ray diffraction methods, direct examination of sols by, 1095
diffraction studies, constitution of hydrous oxide sols from, 1
diffraction studies of chitin, chitosan, and derivatives, 863
spectrography of alkali celluloses, 27
studies of crystallite orientation in cellulose fibers, 343
- Xylose solutions, production of furfural from, 133
- Zeolite crystals, adsorption and diffusion in, 223
- Zinc sulfide, postprecipitation of, with mercuric sulfide, 779

AUTHOR INDEX

- ABRAMSON, HAROLD A., AND TAYLOR, IVON R. The reduction of some adsorbed oxidation-reduction indicators, 519
- ADDLESTON, J. A. *See* Crockford, H. D.
- ALBERT, G. G. *See* Frazer, J. C. W.
- ALEXANDER, LYLE T. *See* Haring, M. M.
- ANDERSON, CLARENCE H. *See* Kobe, Kenneth A.
- ANNETTS, MAY, AND NEWMAN, LORNE. Spectroscopic estimation of adsorbed ions, 187
- BACON, R. CHARLES. A study of the laws governing the cation-exchanging properties of a precipitated aluminum silicate, 747
- BAILEY, EMERSON D. *See* Kraemer, Elmer O.
- BANCROFT, WILDER D. The oxide film on passive iron, 37
The phase rule in colloid chemistry, 43
AND PORTER, JERMAIN D. Kelvin single-potential differences, 1201
- BARTELL, F. E., CULBERTSON, J. L., AND MILLER, MIKE A. Alteration of the free surface energy of solids. I. Vertical-rod method for the measurement of contact angles and preliminary study of effect of heat treatment on magnitude of contact angles, 881
AND MILLER, MIKE A. Alteration of the free surface energy of solids. II. Effect of heat treatment of metals in air, 889
AND MILLER, MIKE A. Alteration of the free surface energy of solids. III. Effect of heat treatment of metals in a vacuum and in several gases, 895
- BARTSCH, CHARLES EDWARD. *See* MacDougall, F. H.
- BECK, FRANCES F. *See* Krantz, John C., Jr.
- BENT, HENRY E., AND KEEVIL, NORMAN B. The viscosity of sodium amalgams, 709
- BREWER, I. *See* Hazlehurst, T. H., Jr.
- BRIDGER, G. L. *See* Scott, Arthur F.
- BRISCOE, H. T., AND GORE, ROBERT C. The dielectric constants of solutions of some organic acids in ethyl alcohol and benzene, 619
- BROUGHTON, GEOFFREY *See* Squires, Lombard
- BROWN, O. W. *See* Huitema, Roy
- BULL, HENRY B., AND MOYER, LAURENCE S. Electrokinetics. XVI. Streaming potential in small capillaries, 9
AND THEIS, ROBERT M. Molecular dimensions from viscosity studies, 125
- BUSWELL, A. M., AND LARSON, T. E. Optical difficulties with the cylindrical cataphoresis cell, 833
- CADY, H. P., AND INGLE, J. D. A comparison of the glass and quinhydrone electrodes for the measurement of the activity of the hydrogen ion in sucrose solutions, 837
- CALKIN, JOHN B. X-ray spectrography of alkali celluloses, 27
- CAMERON, A. E. *See* Reyerson, L. H.
- CAMERON, F. K. Ferric sulfate in aqueous solutions of other sulfates, 689
- CAMPANELLA, JOSEPH L. *See* Parks, W. George
- CARLSON, WARNER W. *See* Pagel, H. Armin
- CARPENTER, ERWIN L. *See* LaMer, Victor K.
- CARR, C. JELLEFF. *See* Krantz, John C., Jr.

- CARRUTHERS, J. C. *See* Roberts, A. L.
CASSEL, HANS M., AND NEUGEBAUER, KURT. The adsorption of the heavier rare gases by mercury, 523
CHENG, L. T. *See* Hartman, R. J.
CHITTUM, JOSEPH F., AND HUNT, HERSCHEL. Liquid ammonia as a solvent. V. Metallic solutions, 581
AND HUNT, HERSCHEL. The adsorption condenser and electromotive force, 1083
See Hunt, Herschel
CHRISTENSEN, L. M. *See* Fulmer, Ellis I.
CLARK, GEORGE L., AND SMITH, ALBERT F. X-ray diffraction studies of chitin, chitosan, and derivatives, 863
CLARK, R. E. *See* Reyerson, L. H.
COLE, A. F. W., AND GORDON, A. R. The diffusion of copper sulfate in aqueous solutions of sulfuric acid, 733
COLLINS, E. M. *See* Menzies, Alan W. C.
COOMBS, C. E. *See* Traxler, R. N.
COX, J. T., JR. *See* Hauser, E. A.
CROCKFORD, H. D., AND ADDLESTON, J. A. The solubility of lead sulfate in aqueous solutions of sulfuric acid at high concentrations, 303
CROWE, M. O'L. *See* Wadsworth, Augustus
CULBERTSON, J. L. *See* Bartell, F. E.
CUNNINGHAM, G. E., GABLER, H. E., AND PEACHIN, W. S. Adsorption of ions and the physical character of precipitates, 1183
CURTIS, HOWARD J. *See* Fricke, Hugo
DAVIS, PHOEBE P. *See* France, Wesley G.
DOUGHTY, EDW. W. *See* Eversole, W. G.
DUBOIS, ROBERT, AND ROBERTS, ALEXANDER HUNTER. An experimental test of the identity of electrokinetic potentials. Electrosmosis and streaming potential measurements with a glass slit, 543
erties of the ternary system ethyl alcohol-glycerin-water, 627
EVERSOLE, W. G., AND DOUGHTY, EDW. W. The diffusion coefficient and apparent radius of the cupric ion in silica gels, 55
FORD, T. F. Surface spreading and surface solution of positively adsorbed substances, 835
FOSTER, R. L. *See* Fulmer, Ellis I.
FOURT, LYMAN, AND SCHMITT, FRANCIS O. Unimolecular films of nerve proteins, 989
FRANCE, WESLEY G., AND DAVIS, PHOEBE PAINE. Adsorption at crystal-solution interfaces. VIII. Influence of dyes and other organic compounds on the crystal habit of barium and lead nitrates, 81
AND DAVIS, PHOEBE P. Adsorption at crystal-solution interfaces. IX. The concentration of foreign substances in solution relative to the quantity adsorbed by the host crystal, 177
FRAZER, J. C. W., AND ALBERT, C. G. Adsorption on chromite catalysts, 101
FREUNDLICH, H., AND JONES, A. D. Sedimentation volume, dilatancy, thixotropic and plastic properties of concentrated suspensions, 1217
FRICKE, HUGO, AND CURTIS, HOWARD J. The determination of surface conductance from measurements on suspensions of spherical particles, 715
FULMER, ELLIS I., CHRISTENSEN, L. M., HIXON, R. M., AND FOSTER, R. L. The production of furfural from xylose solutions by means of hydrochloric acid-sodium chloride systems, 133
AND WILLIAMS, JOHN C. A method for the determination of the wall correction for the falling sphere viscometer, 143
EDGERTON, H. E. *See* Hauser, E. A.
ERNST, R. C., WATKINS, C. H., AND RUWE, H. H. The physical prop-

- potassium *n*-amyl xanthate on chalcocite, 257
- GORDON, A. R. *See* Cole, A. F. W.
- GORE, ROBERT T. *See* BRISCOE, H. T.
- GRUBB, HENRY M. *See* Hunt, Herschel
- HACKERMAN, N. *See* Patrick, W. A.
- HALTON, P., AND SCOTT BLAIR, G. W.
A study of some physical properties of flour doughs in relation to their bread-making qualities, 561
- AND SCOTT BLAIR, G. W. The relationship between conditions governing rupture and flow in flour doughs, 811
- HARING, M. M., AND ALEXANDER, LYLE T. Vapor pressure-water content relation for certain typical soil colloids, 195
- HARKINS, WILLIAM D., AND MOON, ROBERT J. An electronic analysis of some surfaces by means of slow electrons, 941
- AND MYERS, ROBERT J. Polymolecular films: mixed films with two or more components I. Fatty acids and non-polar substances, 959
- HARTMAN, R. J., AND CHENG, L. T. Isoelectric point of glycinin, 453
- HAUSER, E. A., EDGERTON, H. E., HOLT, B. M., AND COX, J. T., JR. The application of the high-speed motion picture camera to research on the surface tension of liquids, 973
- AND REED, C. E. Studies in thixotropy I. Development of a new method for measuring particle-size distribution in colloidal systems, 1169
- HAZLEHURST, T. H., JR., MARTIN, H. C., AND BREWER, L. The creeping of saturated salt solutions, 439
- HILLYER, JOHN C. *See* Lincoln, A. T.
- HIXON, R. M. *See* Fulmer, Ellis I.
- HOAGLAND, EARL J., AND RUTZLER, JOHN E., JR. Adsorption by diatomaceous filters, 215
- HOFFMAN, EVERETT J. *See* MacDougall, F. H.
- HOLT, B. M. *See* Hauser, E. A.
- HOWARD, H. C. The polymeric character of bituminous coal, 1103
- HUGGINS, MAURICE L. Hydrogen bridges in ice and liquid water, 723
- HUITEMA, ROY, AND BROWN, O. W. Tin vanadate as a catalyst in the oxidation of toluene to benzoic acid, 531
- HUNT, HERSHEL, CHITTUM, JOSEPH F., AND GRUBB, HENRY M. Studies of polarization discharges in multiple electrode systems, 239
See Chittum, Joseph F.
- HURD, CHARLES B. Studies on silicic acid gels. VI. Influence of temperature and acid upon the time of set, 21
- INGLE, J. D. *See* Cady, H. P.
- IVANOV, K. N. *See* Kudra, O. K.
- JACOBSON, C. A. Silica fluff, 413
- JENNY, HANS. Simple kinetic theory of ionic exchange. I. Ions of equal valency, 501
- JENSEN, L. B. *See* Urbain, W. M.
- JONES, A. D. *See* Freundlich, H.
- JUNGERS, J. C. The radiochemical decomposition of deutero-ammonia, 155
- KARPATSCHOFF, S., AND POLTORATSKA, O. Cathode polarization as a function of the current density in fused salts, 763
- KEEVIL, NORMAN B. *See* Bent, Henry F.
- KEFFLER, L. J. P., AND MAIDEN, A. M. The solubility relationships in mixtures of brassidic acid with erucic acid, methyl brassidate, and ethyl brassidate, 905
- KING, G. B., AND REDFIELD, H. L. Addition compounds of phosphorous acid with certain organic compounds, 919
- KOBE, KENNETH A., AND ANDERSON, CLARENCE H. The heat capacity of saturated sodium sulfate solution, 429
- KOENIG, F. O. Note on thermodynamic equilibrium in the gravitational field, 373
- KOETS, P. Coacervation of amylophosphoric acid and proteins, 1191

- KOLTHOFF, I. M. Adsorption on ionic lattices, 1027
- AND MOLTZAU, R. Mixed crystal formation of zinc sulfide postprecipitated with mercuric sulfide. The aging of mercuric sulfide and of zinc sulfide, 637
- AND MOLTZAU, R. The postprecipitation of zinc sulfide with mercuric sulfide, 779
- AND TOMSICEK, WM. J. The oxidation potential of the system potassium molybdocyanide-potassium molybdicyanide, and the effect of neutral salts on the potential, 247
- KRAEMER, ELMER O., BAILEY, EMERSON D., AND NICHOLS, J. BURTON. Particle size and optical properties of emulsions, 1149
- KRANTZ, JOHN C., JR., CARR, C. JELLEFF, AND BECK, FRANCES F. A further study of the effect of sugar alcohols and their anhydrides on the dissociation of boric acid, 927
- OAKLEY, MARGARETHE, AND CARR, C. JELLEFF. The effect of certain sugar alcohols and their anhydrides on the dissociation of boric acid, 151
- KUDRA, O. K., AND IVANOV, K. N. Oxidation processes at the cathode, 769
- LAMER, VICTOR K., AND CARPENTER, ERWIN L. The thermodynamic properties of cadmium sulfate in water-ethyl alcohol solutions, 287
- LARSON, T. E. *See* Buswell, A. M.
- LEE, DOROTHY A. *See* Mack, Guilford L.
- LEHL, H. Böhmite and bayerite, 47
- LEIGHTON, ALAN, AND LEVITON, ABRAHAM. Viscosity relationships in emulsions containing milk fat, 71
- LENHER, SAMUEL, AND SMITH, J. EDWARD. A diffusion study of dyes, 1005
- LEVITON, ABRAHAM. *See* Leighton, Alan
- LINCOLN, A. T., AND HILLYER, JOHN C. Quantitative analyses of Liesegang rings, 645
- LIND, S. C., AND LIVINGSTON, ROBERT. Adsorption of radon by glass, 419
- LINHART, GEORGE A. Penetration of solar and cosmic rays into fresh water lakes, 113
- LISSE, MARTIN W., AND SMITH, MARGARET E. A new electrophoresis cell for microscopic observations, 399
- LIVINGSTON, ROBERT. *See* Lind, S. C.
- LOUGHBOROUGH, D. L. *See* Stamm, Alfred J.
- MACDOUGALL, F. H., AND BARTSCH, CHARLES EDWARD. The solubility and activity coefficient of silver acetate in mixed solvents, 649
- AND HOFFMAN, EVERETT J. The solubility of lead bromate and its activity coefficients in solutions of electrolytes, 317
- MACK, GUILFORD L. The determination of contact angles from measurements of the dimensions of small bubbles and drops. I. The spheroidal segment method for acute angles, 159
- AND LEE, DOROTHY A. The determination of contact angles from measurements of the dimensions of small bubbles and drops. II. The sessile drop method for obtuse angles, 169
- MAIDEN, A. M. *See* Keffeler, L. J. P.
- MARTIN, H. C. *See* Hazlehurst, T. H., Jr.
- MASON, L. S. *See* Washburn, E. Roger
- MCBAIN, JAMES W., AND SEARLES, JANET. Mixtures of colloidal electrolytes with uni-univalent salts, 493
- AND SESSIONS, R. F. Activation of redwood and ash-free sugar charcoal in a current of air, 603
- AND STUEWER, R. F. Ultrafiltration through Cellophane of porosity adjusted between colloidal and molecular dimensions, 1157
- AND THOMAS, WINIFRED MCCLATCHIE. Transference numbers of colloidal "ferric hydroxide," 997
- MCDOWELL, M. L. *See* Pearce, J. N.
- MELAVEN, A. D. *See* Parks, L. R.
- MENZIES, ALAN W. C., AND COLLINS, E. M. A comparative method for measuring aqueous vapor and disso-

- ciation pressures, with some of its applications, 379
- MILLER, MIKE A. *See* Bartell, F. E.
- MILLIGAN, W. O. *See* Weiser, Harry B.
- MOLTZAU, R. *See* Kolthoff, I. M.
- MONAGHAN, BETTY. *See* White, H. L.
- MOON, ROBERT J. *See* HARKINS, WILLIAM D.
- MOYER, LAURENCE S. *See* Bull, Henry B.
- MUUS, JYTTE. Carbon dioxide cleavage from dibromomalononic acid, 121
- MYERS, ROBERT J. *See* Harkins, William D.
- NEUGEBAUER, KURT. *See* Cassel, Hans M.
- NEURATH, HANS. The influence of denaturation on the spreading of proteins on a water surface, 361
- NEWMAN, LORNE. *See* Annetts, May
- NICHOLS, J. BURTON. *See* Kraemer, Elmer O.
- NICKERSON, R. F. A study of the sorption of acid sodium oleate, 277
- OATLEY, MARGARETHE. *See* Krantz, John C., Jr.
- PAGEL, H., ARMIN, AND CARLSON, WARNER W. The mechanism of the photochemical reaction between bromine and water, 613
- PARKS, L. R., AND MELAVEN, A. D. Hide substance with hydrogen chloride and ammonia, 471
- PARKS, W. GEORGE, AND CAMPANELLA, JOSEPH L. The solubility of lanthanum in mercury from 0°C. to 50°C., 333
- PATRICK, W. A., AND HACKERMAN, N. Studies on molecular weight changes of sulfur monochloride, 679
- PEACHIN, W. S. *See* Cunningham, G. E.
- PEACOCK, D. H., AND SINGH, ATTAR. The reactivity of halogen compounds. II. The rates of reaction and the energies of activation of 2,4-dinitrochlorobenzene with aromatic primary amines, 669
- PEARCE, J. N., AND McDOWELL, M. L. The activity coefficients of lithium chloride and potassium iodide in ethyl alcohol by the boiling-point method, 845
- PETROVICH, A. *See* van Klooster, H. S.
- PHIPPS, H. E. *See* Reedy, J. H.
- POLTORATSKA, O. *See* Karpatschoff, S.
- PORTER, JERMAIN D. *See* Bancroft, Wilder D.
- PORTER, J. D. *See* Bancroft, Wilder D.
- RAVITZ, S. FREDERICK. The solubilities and free energies of some metallic sulfides, 61
- REDFIELD, H. L. *See* King, G. B.
- REED, C. E. *See* Hauser, E. A.
- REEDY, J. H., AND PHIPPS, H. E. Observations on polymorphism, 89
- REYERSON, L. H., AND CAMERON, A. E. The sorption of bromine and iodine by activated charcoal, 233
- AND CLARK, R. E. The adsorption of complex ammonium ions by silica gel, 1055
- ROBERTS, ALEXANDER HUNTER. *See* Du Bois, Robert
- ROBERTS, A. J., AND CARRUTHERS, J. C. On the U-tube method of measuring electrophoresis, 703
- ROYSTER, P. H. *See* Southard, J. C.
- RUTZLER, JOHN E., JR. *See* Hoagland, Earl J.
- RUWE, H. H. *See* Ernst, R. C.
- SCHMITT, FRANCIS O. *See* Fourn, Lyman
- SCHUHMAN, REINHARDT, JR. *See* Gaudin, A. M.
- SCOTT, ARTHUR F., AND BRIDGER, G. L. The apparent volumes and apparent compressibilities of solutes in solution. III. Unsaturated and super-saturated solutions of calcium nitrate, 461
- SCOTT, BLAIR, G. W. *See* Halton, P.
- SEARLES, JANET. *See* McBain, James W.
- SEN, BINAYENDRA NATH. The formation of hiesegang rings in the presence of precipitates, 369
- SESSIONS, R. F. *See* McBain, James W.
- SHAFFER, P. A. Catalysis of ionic oxidation-reduction reactions by dyes and its probable mechanism, 1021

- SINGH, ATTAR. *See* Peacock, W. H.
- SISSON, WAYNE A. X-ray studies of crystallite orientation in cellulose fibers. II. Synthetic fibers from bacterial cellulose membranes, 343
- SMITH, ALBERT F. *See* Clark, George L.
- SMITH, J. EDWARD. *See* Lenher, Samuel
- SMITH, MARGARET E. *See* Lisse, Martin W.
- SOUTHARD, J. C., AND ROYSTER, P. H. The thermal dissociation of calcium carbonate, 435
- SQUIRES, LOMBARD, AND BROUGHTON, GEOFFREY. The gelation of bentonite suspensions, 1041
- STAMM, ALFRED J., AND LOUGHBOROUGH, D. L. Molecular properties of lignin solutions from viscosity, osmotic pressure, boiling-point raising, diffusion, and spreading measurements, 113
- STUEWER, R. *See* McBain, James W.
- TAYLOR, IVON R. *See* Abramson, Harold A.
- THEIS, ROBERT M. *See* Bull, Henry B.
- THOMAS, WINIFRED McCLATCHIE. *See* McBain, James W.
- TISELIUS, ARNE. Adsorption and diffusion in zeolite crystals, 223
- TOMSICEK, WM. J. *See* Kolthoff, I. M.
- TOWER, OLIN F. Liesegang rings of manganese sulfide. II, 599
- TRAXLER, R. N., AND COOMBS, C. E. The colloidal nature of asphalt as shown by its flow properties, 1133
- URBAIN, W. M., AND JENSEN, L. B. Soaps: electric charge effects and dispersing action, 821
- URBAN, FRANK. *See* White, H. L.
- VAN KLOOSTER, H. S., AND PETROVICH, A. The flocculation of the stannic oxide sols, 591
- VOET, ANDR. Colloidal solutions in concentrated electrolytes, 307
- WADSWORTH, AUGUSTUS, AND CROWE, M. O'L. A preliminary study of the absorption spectra of cephalin, lecithin, and selected antigens, 739
- WARK, ELSIE EVELYN. *See* Wark, Ian William
- WARK, IAN WILLIAM. The physical chemistry of flotation. VII. Trimethylcetylammmonium bromide as a flotation agent, 661
- AND WARK, ELSIE EVELYN. The physical chemistry of flotation. VIII. The process of activation, 799
- WASHBURN, E. ROGER, AND MASON, L. S. Specific heats and related properties of the binary system methyl alcohol-toluene, 481
- WATKINS, C. H. *See* Ernst, R. C.
- WEISER, HARRY B., AND MILLIGAN, W. O. The constitution of hydrous oxide sols from x-ray diffraction studies, 1
- AND MILLIGAN, W. O. The direct examination of sols by x-ray diffraction methods, 1095
- AND MILLIGAN, W. O. The mechanism of the coagulation of sols by electrolytes. VI. Cupric ferricyanide sol, 1071
- WHITE, H. L., AND MONAGHAN, BETTY. Factors influencing adsorption at surfaces of red cells, 1063
- MONAGHAN, BETTY, AND URBAN, FRANK. Stream potentials and d.c. surface conductivities in small capillaries, 207
- WILLIAMS, JOHN C. An hypothesis concerning bacteriophagy, 477
- See* Fulmer, Ellis I.

INDEX TO NEW BOOKS

- Abridged Scientific Publications from the Kodak Research Laboratories, 936
- BJERRUM, N. Inorganic Chemistry, 859
- BRIDGMAN, P. W. The Nature of Physical Theory, 937
- BRISCOE, HERMAN T. Structure and Properties of Matter, 424
- BUZÁGH, A. v. Kolloidik. Eine Einführung in die Probleme der modernen Kolloidwissenschaft, 933
- CLAYTON, WILLIAM. The Theory of Emulsions and their Technical Treatment, 936
- Collected Scientific Papers of Sir William Bate Hardy, F.R.S., 856
- Colloid Symposium Monograph, 287
- DE BOER, J. H. Electron Emission and Adsorption Phenomena, 421
- DOCZEKAL, [redacted] collaboration with H. Pitsch, [redacted] neue thermische Daten und Gleichgewichtskonstante, 290
- DOLE, [redacted] M. The Principles of Experimental and Theoretical Electrochemistry, 288
- ELLIS, O. C. DE C., AND KIRKBY, W. A. Flame, 701
- FARKAS, ADALBERT. Orthohydrogen, Parahydrogen and Heavy Hydrogen, 288
- FERCHL, F., AND SÜSSENGUTH, A. Kurzgeschichte der Chemie, 938
- FURNAS, C. C. The Next Hundred Years: The Unfinished Business of Science, 697
- GLASSTONE, S., AND HICKLING, A. Electrolytic oxidation and Reduction: Inorganic and Organic, 697
- Gmelins Handbuch der anorganischen Chemie. Aluminum, 702, 934
- Gmelins Handbuch der anorganischen Chemie. Stickstoff, 428, 701
- Gmelins Handbuch der anorganischen Chemie. Uran und Isotope, 934
- GODDARD, E. D. Fundamental Experiments in Chemistry, 937
- GRÜTZNER, A. Eisen- und Stahlliegierungen. Patentsammlung. 1 Ergänzungsheft, 428
- GRÜTZNER, A., AND APEL, G. Aluminium-Legierungen, 701
- HASCHEK, E., AND HANFINGER, MAX. Monographien aus dem Gesamtgebiete der Mikrochemie. Farbmessungen, Theoretische Grundlagen und Anwendungen, 423
- HICKINBOTTOM, W. J. Reactions of Organic Compounds, 702
- HILDEBRAND, JOEL H. Solubility of Non-electrolytes, 700
- HITCHCOCK, FRANK LAUREN, AND ROBINSON, CLARK SHOVE. Differential Equations in Applied Chemistry, 937
- JELLINEK, K. Lehrbuch der physikalischen Chemie, 858
- JÖRGENSEN, H. Wasserstoff-Ionenkonzentration (pH), 427
- Journal of the Institute of Metals, 427
- KAYE, G. W. C., AND LABY, T. H. Tables of Physical and Chemical Constants and Some Mathematical Functions, 938
- KOLTHOFF, I. M., AND SANDELL, E. B. Textbook of Quantitative Inorganic Analysis, 858
- KRZIL, FRANZ. Adsorptionstechnik, 857
- LOWRY, T. MARTIN. Optical Rotatory Power, 287

- MACDOUGALL, FRANK H. *Physical Chemistry*, 939
- MENZER, G. *Stereoscopic Drawings of Crystal Structures*, 934
- Metallurgical Abstracts (General and Non-ferrous), 427
- MILLIKAN, ROBERT A. Electrons (+ and -), Protons, Neutrons and Cosmic Rays, 289
- MITCHELL, S. A. *Eclipses of the Sun*, 935*
- MITTASCH, ALWIN. Ueber katalytische Verursachung im biologischen Geschehen, 699
- OFFENHEIMER, CARL. *Die Fermente und ihre Wirkungen*, 700
- PARSONS, T. R. *Fundamentals of Biochemistry in Relation to Human Physiology*, 700
- PARTINGTON, J. R. *Origins and Development of Applied Chemistry*, 421
- PERRET, FRANK A. The eruption of Mt. Pélee, 1929-32, 425
- PETERS, JOHN P. *Body Water—The Exchange of Fluids in Man*, 422
- Phenomena of Polymerisation and Condensation, The, 855
- RADLEY, J. A., AND GRANT, JULIUS. *Fluorescence Analysis in Ultraviolet Light*, 855
- Reports on Progress in Physics, 933
- SCHÜLEIN, JULIUS. *Die Bierhefe als Heil-, Nähr-, und Futtermittel*, 424
- SNELL, FOSTER DEE, AND SNELL, CORNELIA T. *Colorimetric Methods of Analysis*, 699
- SPONER, H. *Molekülspektren und ihre Anwendung auf chemische Probleme*, 861
- STEWART, A. W. *Recent Advances in Organic Chemistry*, 938
- Structure of Metallic Coatings, The, 425
- TERTSCH, H. *Das Kristallzeichnen auf Grundlage der stereographischen Projektion*, 426
- TILDEN, SIR WILLIAM A. *Chemical Discovery and Invention in the Twentieth Century*, 861
- TIMMERMANS, JEAN. *Les Solutions Concentrées. Théorie et Applications aux Mélanges Binaires de Composés Organiques*, 699
- Veröffentlichungen aus dem Kaiser Wilhelm-Institut für Silikat-Forschung in Berlin-Dahlem, 860
- VON LAUE, M. *Die Interferenzen von Röntgen und Elektronenstrahlen*, 860
- VON LAUE, M., AND VON MISES, R. (editors). *Stereoscopic Drawings of Crystal Structures*
- WATERS, WILLIAM A. *Aspects of Organic Chemistry*
- WEBB, T. J. *Elementary Principles in Physical Chemistry*, 940
- WEISER, H. B. *Inorganic Colloid Chemistry. II. The Hydrous Oxides and Hydroxides*, 698
- WYCKOFF, RALPH W. G. *The Structure of Crystals*, 422

Indian Agricultural Research Institute (Pusa)
LIBRARY, NEW DELHI-110012

This book can be issued on or before.....

Return Date	Return Date